KVL AgroTechnology

# SENSING TASTE OF FRUITS AND VEGETABLES USING NEAR INFRARED (NIR) TECHNOLOGY

**'Master Thesis'**


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# *'Sensing taste of fruits and vegetables using near infrared (NIR) technology'*

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## Preface

This study is submitted in order to achieve a 'M.Sc. degree' in 'Agricultural Sciences' from 'Department of Agricultural Sciences, AgroTechnology section / Postharvest Technology', at the Royal Veterinary and Agricultural University (KVL), Copenhagen, Denmark.

The M.Sc. program was funded by DANIDA (Danish International Development Assistance).

The aim of this study was to extend the recent theoretical and experimental background about NIR technique as a non-destructive quality sensor. Based on the success of NIR spectroscopy for predicting the internal quality parameters, like soluble solids content and acidity, this study is addressing the feasibility of NIR for detecting taste of fruits. Ongoing work will evaluate the possibility of designing a NIR taste sensor.

The thesis is based on a literature review and experimental work described in eight chapters and an appendix. The appendix includes most of the statistical glossaries that are important to understand the multivariate analysis that was used in this thesis.

Two articles, which have been submitted to two international journals, will give a comprehensive idea about this study.

## Acknowledgments

I am greatly indebted to many people for their support and encouragement during the period this work was done.

I sincerely thank Danish Government – Ministry of Foreign Affairs / DANIDA (**Dan**ish **I**nternational **D**evelopment **A**ssistance), for offering me such a golden opportunity to study in KVL University, by financing this study through the fellowship programs. In this regards a special thank goes to DFC (**D**anida **F**ellowship **C**enter) staff who tried their best to provide comfortable life, and for their efficient management of both social and academic aspects of my program while in Denmark. Many thanks to DFC café staff members for their kindness and cooperation. Deep thanks to 'Ms. Mona Duzdar' at the Royal Danish Representative Office in Palestine for her solicitude and help.

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Last but not least, I would like to thank all of my colleagues for their support and kindness during my study.

## Abstract

This project concerns the feasibility of using near infrared (NIR) technology for sensing taste of fruits and vegetables. This study was conducted based on the known non-destructive ability of NIR to assess some internal quality parameters of fruits and vegetables, like soluble solid contents (SSC), acidity and other chemical components.

Ongoing work will evaluate the possibility of designing a NIR taste sensor. This sensor can be used online in fruit grading (according to their taste quality) in warehouses and public fruit markets.

Taste of any fruit is considered to be composed from SSC, acidity and characteristic taste parameters of the fruit (distinguished chemicals). The possibility of distinguishing between two different varieties (of the same fruit) having the same SSC/acidity values means that SSC and acidity are eliminated leaving only the characteristic taste parameters in both varieties to be detected.

A NIR spectrometer with photo diode array (PDA) detector and fiber optics was used for spectra measurement. Non-destructive prediction and classification was based on optical reflectance in NIR range (700-1100 nm).

Three experiments were carried out, one for plums and two for apples. Two different varieties of same fruit were used in each experiment.

A reasonable correlation between NIR reflectance and a number of quality parameters was achieved. Also, it was found that it is possible to classify two varieties of fruits. Furthermore, NIR spectroscopy could classify two varieties even when they had the same ratio of SSC and acidity (the verification of the study).

Two varieties of plums (Reine Claude and Blackamber), which had the same ratio of SSC and acidity, were both correctly classified in 92.8% of the cases at 5% significant level.

Golden Delicious and Jonagold apples were correctly classified in 90% and 83.4% of the cases respectively at 5% significant level. Also, Aroma and Elstar apple samples, which had the same ratio of SSC and acidity, were correctly classified in 100% and 85% cases respectively at 10% significant level.

Thus, it can be concluded that NIR technology has a high potential in sensory science for sensing taste of fruits.

## Dedication

*To my family; and*

*To everyone who has helped and supported me to reach this stage.*

# Contents

## List of Abbreviations

| | |
|---|---|
| A | Absorbance. |
| AIS | Alcohol Insoluble Solids. |
| CCD | Charge Couple Device. |
| CV | Coefficient of Variation. |
| DM | Dry Matter. |
| GMP | Disodium Guanylate. |
| IMP | Disodium Inosinate. |
| KVL | The Royal Veterinary and Agricultural University |
| LDPS | Light Addressable Potentiometric Sensor. |
| MLR | Multiple Linear Regression. |
| MMS | Monolithic Miniature Spectrometer. |
| ms | Milli Second. |
| MSG | Monosodium Glutamate. |
| NIR | Near Infrared. |
| nm | Nanometers. |
| OD | Optical Density. |
| OEM | Original Equipment Manufacture. |
| PCA | Principal Component Analysis. |
| PCR | Principal Component Regression. |
| PCs | Principal Components. |
| PDA | Photo Diode Array. |
| PLS | Partial Least Square. |
| r | Correlation Coefficient. |
| R | Reflectance. |
| RMSEC | Root Mean Square Error of Calibration. |
| RMSEP | Root Mean Square Error of Prediction. |
| SDev | Standard Deviation. |
| SEC | Standard Error of Calibration. |
| SEP | Standard Error of Prediction (or Performance). |
| SIMCA | Soft Independent Modeling of Class Analogies. |

| | |
|---|---|
| SSC | Soluble Solids Content. |
| T | Transmittance. |
| TSS | Total Soluble Solids. |
| UV | Ultra Violet. |
| VIS | Visible. |

# 1. Introduction

The quality[1] of fruits and vegetables is becoming more important for consumers as well as for producers. An increased number of consumers have been recently noticed to buy a prime quality with a better taste upon higher price.

Quality measurement techniques have been developed during recent years. Some of them are destructive and others are non-destructive. The trends all over the world now is to develop non-destructive techniques for measuring quality attributes of fruits and vegetables. These techniques are fast executing, requires only limited sample preparation and are easy to use in process control and grading systems (Lammertyn *et al.*, 2000).

NIR spectroscopy is one of these techniques. It has been successfully used as a sensor to predict some of the quality parameters like soluble solids content (SSC), acidity and dry matter in different agricultural commodities.

This study is addressing the feasibility of using NIR spectroscopy for sensing taste of fruits and vegetables, based on known NIR ability to predict SSC, acidity and chemicals components. Taking into consideration that fruit taste is the major asset of fruit quality (Blanke, 1996).

In this study, NIR reflectance and chemical characteristics of two different varieties of the same fruit was studied. Prediction of some quality parameters was investigated. The possibility of classification of two varieties was carried out. Then, the possibility of classification samples from both varieties having the same ratio of SSC and acidity were investigated, to ensure that the classification was not based on SSC and acidity, but on the characteristic taste parameters in each variety. The idea being that if this

[1] 'The term quality implies the degree of excellence of a product or its suitability for a particular use. Quality is a human construct comprising many properties or characteristics. Quality of produce encompasses sensory properties (appearance, texture, taste and aroma), nutritive values, chemical constituents, mechanical properties, functional properties and defects' (Abbott, 1999).

works, it will give an indication that NIR detects the taste of fruits, and this will open a wide range for designing a NIR taste sensor in the future.

The research was conducted on plums and apples, due to their economically importance, and apple availability in different varieties all over the year in Palestine (Abu-Khalaf, 2000).

The goal of this study is to build a background for taste sensing. It is a step in a long research process for identifying characteristic taste parameters for each fruit and vegetable.

# 2. NIR technology

*This chapter presents a literature review of NIR technology: its history, principles, background, its powerful capacity in food analysis and its use as a non-destructive quality measurement for fruits and vegetables.*

## 2.1. Background and principles of NIR

Herschel recognized NIR energy at the beginning of the nineteenth century. It has been proposed that in recognition of his historic discovery, the NIR region between 780 and 1100 nanometers (nm) should be termed the 'Herschel infrared' (Davies, 1997). But traditionally spectroscopists have avoided this region of the spectrum for analytical use because of the difficulty of interpreting the complex overlapping absorbance peaks and because of its relatively low energy compared with the visible region (Scotter, 1990). Figure 1 shows the NIR in the electromagnetic spectrum.

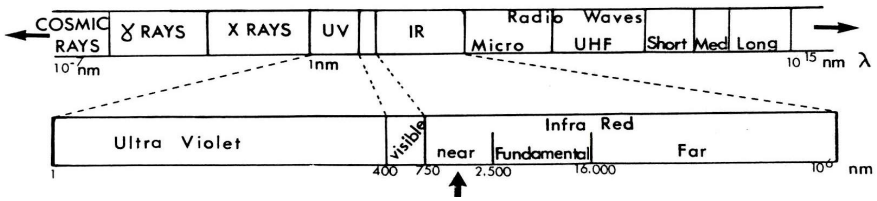


*Fig. 1. NIR in the electromagnetic spectrum.*
Source: Davies, 1982.

Two advances were necessary before the potential analytical power of NIR was recognized. The first was the development of a detector with sufficient sensitivity to detect the low energy of NIR radiation and provide sufficiently high signal to noise absorbance responses combined with high signal/noise instrumentation. The second requirement was for high capacity computers needed for mathematical manipulation to ease out specific chemical information form the complex spectra (Scotter, 1990).

In the 1960s, the name of Karl Norris from the US Department of Agriculture (USDA) laboratories at Beltsville, Kansas, became synonymous with the exploitation of NIR analytical instrumentation for the grain industry (Scotter, 1990). Norris and his team made a very important contribution to the development of data treatment

techniques which make it possible to extract information from spectrophotometeric data (curves), since they found that diffuse reflectance (R), and diffuse transmittance (T), do not vary linearly with the concentration of an absorbing component in the material, therefore, if a linear correlation between NIR measurement and the concentration of an absorber is desired certain mathematical treatment of the reflectance or transmittance data are required. The conversion of data to log (1/R) or log (1/T) gives adequate linearity between concentration of constituent and the measured optical parameter. Some researchers have found that Fourier analysis can be used with several advantages for NIR spectrum, since the NIR spectrum can be transformed into a Fourier series and then analyzed only on the Fourier domain (Chen, 1996).

Over the last forty years, NIR has been used in a wide variety of industrial contexts, including the chemical and pharmaceutical industries. The technique has been used most commonly and successfully in the grain and flour industries. In common with all spectroscopic methods of analysis, NIR spectroscopy depends upon the prime principle that radiation interacts with matter to produce a response, which through appropriate instrumentation can be displayed as an absorbance spectrum. NIR radiation is absorbed or reflected according to the degree, and way, in which the bonds between atoms of dissimilar mass are deformed. One of the important differences between NIR analysis and other spectroscopic methods is that NIR is based on measurements of reflected energy rather than of energy transmitted through the sample. The quantitative and qualitative use of NIR spectroscopy analysis depends upon the Beer-Lambert[2] relationship, which states that absorption is proportional to the concentration, and shows that the log reciprocal absorbance is directly related to the path length of light through the sample. Although demonstrated in the context of transmission of energy through liquids, with the mathematical treatment available, the Beer-Lambert relationship is an adequate approximation for the generation of quantitative or qualitative data from diffuse reflectance spectra of slurry materials or solid powdered (Davies, 1982; Scotter, 1990; Shadow, 1997).

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[2] $\log(I_o/I)=K*C*L$. Where I:intensity of transmitted light, $I_o$: intensity of incoming light, K: absorbance index, C: solution concentration, L: light length through solution (Simonsen, 1994).

Some of the practical applications that the NIR spectrum analyzer has successfully been used for are:

- Classification of tobacco types and identify native grown tobacco (Hana *et al.*, 1997);
- Measuring moisture, protein and fat (the three major constituents) in food processing (Kurowski *et al.*, 1998);
- Identify rice variety, even though accuracy of identification needs to be improved (Kwon and Cho, 1998);
- NIR can predict Warner Bratzler shear force values of longissimus steaks (this can be extended to non-destructively prediction of the beef meat tenderness at the processing plant level) (Park *et al.*, 1998);

Thompson (1996) stated that NIR spectrum analyzer has also successfully been used for:

- Soil moisture content;
- Moisture content in crops;
- Nitrogen and calcium concentration of pear fruit peel;
- Milk and feed composition;
- A useful tool for quality control in processing industry; and
- Measuring the internal qualities, firmness, acidity and soluble solids content of fruits (the most related application for this thesis).

## 2.2. Why NIR?

The general reasons for widely using of NIR technique as a form of analysis in the past few years and until now are (Shadow, 1997):

a) NIR is extremely fast (the most useful aspect of NIR) providing results for multiple parameters in seconds;
b) NIR instruments are generally easy to operate allowing for non-technical users;
c) NIR provides results similar in accuracy to the reference methods to which it is calibrated;
d) Calibration may be shared among similar instruments;
e) There is little or no sample preparation required for NIR technique;
f) NIR technique is safe, environmental friendly and requiring no chemicals;

g) NIR technique is very economical, as there are no chemical purchase or disposal costs;
h) NIR can be used for solid and liquid analyses; and
i) NIR is ideal for complex matrices, in which category most food would fall.

## 2.3. Why NIR for foods?

NIR spectroscopy is uniquely qualified to provide analysis capabilities to the food and related industries, through its interaction with the organic molecular material of foodstuffs. Most food is organic, containing C-H, C-O-H and C-N-H, etc. These bonds interact in a measurable way with the NIR portion of the spectrum. NIR light is energetic enough to bring atoms within a molecule in vibration relative to each other. These interactions occur at the speed of light providing extremely rapid information gathering capabilities. NIR range is the only electromagnetic spectrum that this particular measurable interaction occurs in. NIR creates a faster, safer work environment and does not require chemicals (Shadow, 1997; Timmermans, 2000).

## 2.4. NIR as a non-destructive technique for detecting the internal quality of fruits and vegetables

NIR technology has successfully implemented throughout the food industry as a non-destructive method for analysis the ingredients of organic products, also it presents a very promising future for fruit and vegetable quality control. NIR (800-2500 nm) spectroscopy success reasons are mainly linked to its speed and its ease of implementation. NIR spectra contain information of harmonic and combination bands of functional groups vibrations. These absorption bands are weak, which allows the radiation to penetrate into the fruit. These bands are also very overlapped and require powerful chemometric methods for data processing (Bellon, 1993; Schmilovitch *et al.*, 2000).

Bellon and Sevila (1993) stated that many researchers in the eighties have proved that NIR was a good technique to measure sugar content in a non-destructively way. Researchers worked on many fruits and vegetables, such as onions, peaches, apples

and melons. These studies were done either in the so-called 'near-near infrared' i.e. in the 700-1100 nm range or in the classical 'near-infrared' i.e. the 1200-2500 nm range. Except in the case of whole melons, where the skin was too thick, results were very encouraging with correlation better than 0.95 and low standard error (inferior to 1%). In all experiments, the measurements (spectra) were collected in a non-destructively way, i.e. through the skin, within several seconds or several minutes, by a rotating monochromator. A development of a high speed NIR spectrum was needed.

A new ultra fast NIR spectrometer, which is suitable for sugar analysis in fruits, was developed by Bellon-Maurel (1992). She used a wavelength range between 800-1050 nm to build a model for sugar measurement using a charge couple device (CCD) camera instead of the standard detector for a spectrophotometer, which is a photon multiplier detector (Lammertyn *et al.*, 1998). This new spectrometer is a real-time spectrometer equipped with fiber optics and an array camera, which can match the time requirement for an on-line inspection. The characteristics of this system which make it especially suited to sugar content measurement in fruits are (Bellon, 1993):

- It is fast (25 images/ second);
- Durable (no moving parts);
- Low-cost (regular CCD cameras); and
- Can be multiplexed onto as much as 20 points.

The spectra were analyzed by multivariate methods and yielded good results for sugar content in apples. It was possible to sort 88 apples (different varieties), according to their sugar content, into three categories of maturity with 83% of performance. The optode can be implemented in on-line inspection (Bellon and Sevila, 1993).

The standard error of prediction (SEP) in this device was 2.4 g/l of glucose (Moons *et al.*, 2000).

Figures 2 & 3 show CEMAGREF array-detector optic spectrometer, which was developed by Bellon-Maurel.

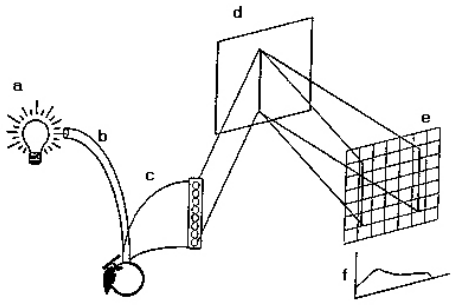


*Fig. 2. The components of CEMAGREF array-detector fiber optic spectrometer.*
Where: a) source, b) emitting, c) collecting branch of the fiber optics bundle, d) grating, e) detector; and f) spectrum.

Source: Bellon, 1993.

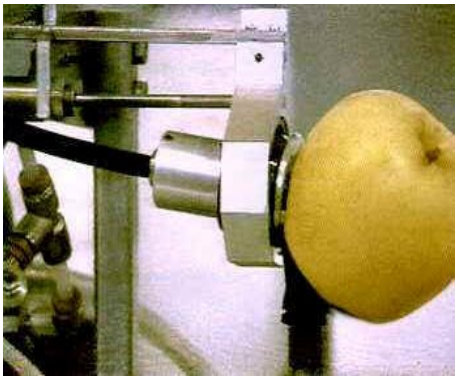

*Fig. 3. The CEMAGREF array-detector fiber optic spectrometer.*

Source: CEMAGREF, 2000.

NIR in the range of 700-1100 nm is promising and more useful for intact foods due to the following facts (Carlini *et al.*, 2000; McGlone and Kawano, 1998;Walsh *et al.*, 2000):

1. Radiation can penetrate much further in fruit of many different species;
2. The corresponding instrumentation is low cost and suited to process control and portable enough for in situ field measurements;
3. The bands are ascribed to the third and forth overtones of O-H and C-H stretching modes and are expected to be separated due to anharmonicity;
4. Lower absorbance at these wavelengths allows for transmission optics; and
5. Water absorbance peaks are less strong and broad and the risk to mask spectral information correlated to low concentration constituents is weak.

Thyholt and Isaksson (1997) stated that NIR is strongly sensitive to water.

Wavelengths in the range of 900-920 nm have been related to sugar content in onion and peach, and wavelengths around 970 nm were used in the regression equation for water content in peach. Recently, many scientists used various wavelengths in their models, since various characteristics of the fruits are taken into account when a number of wavelengths are selected in the regression models (Ventura *et al.*, 1998).

Furthermore, the percentage of dry matter (% DM) of intact onion, cv. *'Allium cepa L'*, was determined by NIR spectroscopy, with a high correlation, above 0.995, using transmission mode and wavelength between 700-1000 nm. The nominal wavelength used to determine the regression equation was associated with a broad carbohydrate absorption band in the vicinity of 906 nm, and maximum absorption occurs at 918 nm. That means, NIR method can be interpreted as a measurement of carbohydrate. This agree with the fact that at least 82% of the dry matter in low and high dry matter onions is carbohydrate, primarily in the form of fructans, fructose, glucose, sucrose and fiber (Birth *et al., 1985;* Dull *et al.,* 1989).

Apple firmness was investigated by NIR, but a limited success was achieved due to changes in pectin and water absorbance bands in the vicinity of 1900 nm. The NIR studies were only in the range of 1100-2400 nm, but there is a pectin absorbance band at around 980 nm that has been identified in NIR spectra for apple and citrus pectin (Cho *et al.* cited by McGlone and Kawano, 1998).

Lovasz *et al.* (1994) investigated the acceptability of NIR transmission spectroscopy for the prediction of six quality factors of apples (firmness, refractive index, pH, titratable acid, dry matter and alcohol insoluble solids (AIS) contents). A certain relationship seems to exist between the maturity and NIR transmission spectra of the apple.

Kupferman (1997) stated that fruit firmness is generally very difficult to measure, since many factors are involved. Theoretically it is possible that scattering of light within the fruit may relate to firmness.

Ventura *et al.* (1998) used a portable NIR spectrophotometer to estimate soluble solid content in stored apple fruits after post harvest storage, and it was concluded that it

could be possible to use a portable NIR spectrophotometer in the orchard with some difficulties, like temperature and light.

Cho *et al.* (1998) stated that the sweetness score of apple fruit could be determined by NIR spectroscopy.

Also, NIR technique has been used to assess juiciness in apples (Grummisch *et al.* cited by Ortiz *et al.,* 2001).

Lammertyn *et al. (*1998) used successfully visible and NIR spectroscopy (380-1650 nm) as a non-destructive technique for measuring internal apple's (Jonagold variety) quality (pH, soluble solids and stiffness factor). Multivariate calibration techniques, such as principal component analysis (PCA), principal component regression (PCR), and partial least square (PLS) were used for the statistical analysis of the data and the construction of the prediction models. The prediction models indicate a good to excellent prediction performances. The best pH model has a SEP of 0.068 and a correlation (r) between predicted and measured value of 0.93. This model has shown that pH has a physio-chemical background. Stiffness' model has a SEP of 2.49 and an r-value of 0.90. The soluble solids content (SSC) model has a SEP of 0.61 and an r-value of 0.82. The prediction performance of the model of elastic modulus was not satisfactory, SEP was 0.26 and r-value of 0.75.

Peirs *et al.* (2000) used NIR spectroscopy to measure internal quality factors of apples to support the determination of their optimal picking date. A good correlation was obtained between Streif index[3] with the spectra. So, NIR spectroscopy offers a fast and convenient method to monitor the maturity of the fruit before harvest and can be a valuable tool for the determination of the optimal harvest date.

Moons *et al.* (2000) got good results for prediction of several internal parameters, like brix, acidity and hardness, for 300 apples from different varieties, using NIR

[3] Streif index = firmness/ (starch conversion * soluble solid content).
This index is an indication for picking time.

spectroscopy within a range of 400-1700 nm. PLS and MLR statistical techniques were used in data analysis.

Non-destructive NIR methods have been used to detect bruises on apples. Spectroscopic studies have been shown that freshly bruised tissue has a lower reflectance than non-bruised tissue for the visible through NIR wavelengths. Specific wavelengths for distinguishing between the bruised and the non-bruised tissue on peeled apples were identified (Lammertyn *et al.*, 1998).

Mealiness as well as other internal defects inside apples could be detected and measured in Cox and Jonagold varieties through the VIS/NIR transmission spectroscopy (Merurens and Fethi, 2000).

Also, NIR spectroscopy was used in tomatoes' quality assessment. It was found that acceptable prediction of quality index, including total soluble solid (TSS), titratable acidity and color (-a/b value) could be achieved (Hong and Tsou, 1998).

By using NIR to measure chlorophyll content and couple this information with x-rays, green tomato fruit can be ranged in maturity from immature green to advance mature green tomato (Thai *et al.*, 1997).

Detection of tomato's surface defects has been achieved by measuring reflectance at 670 and 960 nm (Moini and O'Brein cited by Laykin *et al.*, 1999).

Peiris *et al.* (1998) used NIR absorbance spectrometry to predict the SSC of processing tomatoes non-destructively. Since SSC is a prime concern in fresh market tomatoes due to the important contribution of sugars and acids to the overall flavor of the fruit. In tomatoes, 55%-65% of the total SSC is reducing sugars (fructose and glucose), sucrose is about 0.1% on a fruit mass basis, citric and malic acids consists 10%-15% of SSC. The remaining compounds are minor organic acids, amino acids, lipids and minerals. Most of these organic compounds absorb NIR due to the presence of functional groups (e.g. R-OH, R-$NH_2$, R-CH, R-$CH_2$ and R-$CH_3$) on the molecules.

Dull *et al.* (1989) used NIR spectroscopy to predict dry matter (DM) in sliced and intact potato tubers, cv. *'Russet burbank'*. They used direct transmittance mode, and wavelength range between 800-1000 nm. There was a high correlation for DM prediction, since (r) values between DM and spectral were -0.975, -0.952 and 0.918 for thin slices, thick slices and intact tubers respectively. Krivoshiev *et al.* (2000) stated that these authors noted that the inclusion of the peel in the light path does not change the fundamental dependencies between the spectral and chemical data. Krivoshiev *et al.* (2000) don't agree with them in this point, since Krivoshiev *et al.* (2000) think that the tubers were well peeled and they were from the same variety.

For cantaloupe and honeydew melons, NIR was used to determine the soluble solids in these fruits (Chen, 1996). An instrument based on NIR reflectance technique was used for detecting soluble solids in honeydew melons. This instrument used tilting-interference filter technology for wavelength scanning and a silicon detector with preamplifier for sensing radiation that has passed through the melon flesh. The standard error of calibration was (0.82) soluble solids when compared with the laboratory refractometer measurements (Dull *et al.,* 1992).

For vining peas and sweetcorn product quality factors assessment of product, NIR reflectance spectroscopy was used. The calibration results for alcohol insoluble solids (AIS)[4] in peas and sweetcorn, and Tenderometer measurement and sensory assessment for both vegetables indicate that the work will find industrial application (Scotter, 1998).

Prediction of firmness, DM and SSC of postharvest kiwifruit were developed from NIR interactance measurements using a narrow spectral range from 800-1100 nm. Firmness is considered the primary indicator of kiwifruit eating ripeness. The SSC of kiwifruit is often believed to be linked to consumer taste preference, although a close linkage has not been unequivocally demonstrated or reported. SSC and DM could both be predicted with a very good accuracy using NIR technology. Taking into consideration that the application of NIR technology with the kiwifruit industry, for DM and SSC estimation on ripening kiwifruit, will depend on both the development

[4] The measurement of AIS relates to the conversion of sugars to starch in peas and sweetcorn.

of appropriate cost effective instrumentation and also on demonstration that these constituents mean something in terms of consumer taste preferences. Firmness prediction was not promising, and suggestions for influence of second correlations were proposed (due to fruit characteristic that are not directly related to the firmness) (McGlone and Kawano, 1998).

For mangoes and pineapples, NIR measurements have shown an adequate correlation for soluble solids. Results for acidity and firmness were also encouraging for mangoes, but further studies are needed (Kouno *et al.*, 1993). In these experiments, NIR measurement was achieved by using a Nireco model 6500 near-infrared spectrophotometer, by placing the fruit so that the light beam on the surface was at right angles to the fruit surface, which was covered with a black cloth to avoid the influence for external light. Four places around the equator of the fruit were selected and the NIR beam was irradiated at 2 nm intervals, from 400-2500 nm, onto the fruit and the average absorbance was measured. Fruit firmness, acidity and soluble solids content were measured directly afterwards on the same fruit, and adequate correlation were shown between the NIR measurements and SSC for both mangoes (multiple regression coefficient of 0.954) and pineapples (multiple regression coefficient of 0.825). Results for acidity and firmness were also encouraging for mangoes: a multiple regression coefficient of 0.856 for acidity, 0.949 for the firmness of the unpeeled fruit and 0.920 for the peeled fruit. For pineapples the multiple regression coefficient was 0.686 for the acidity, 0.460 for firmness of unpeeled fruit and 0.568 for peeled fruit (Thompson, 1996).

Also, Schmilovitch *et al.* (2000) evaluated the non-destructive use of NIR spectroscopy reflectance in measuring the physiological properties (TSS, acidity, firmness and storage period) of mango fruit, cv. '*Tommy atkins'*. It was concluded that NIR provided good estimates for maturity indices, especially for TSS.

Slaughter (1995) investigated the possibility of using visible and NIR spectroscopy (400-1100 nm) to measure non-destructively the internal quality of peaches and nectarines as characterized by their soluble solids, sucrose content, sorbitol content and chlorophyll content. All of these factors had been correlated with 92%, 87%, 88% and 97% respectively.

NIR spectrophotometer was used for sampling (separating and sorting) fresh dates by detection of ripening and maturity, since fruits which don't ripen properly but are shipped together with ripe dates cause deterioration of the quality. NIR with wavelength of 650-3000 nm was used, which are within the range absorbed by the most organic materials. Analysis by means of the NIR method was tested and found capable of detecting dates with high sugar content or low moisture content, which are the ones that will ripen. Prediction results provided correlation coefficients of 0.91-0.95 for moisture content and of 0.82-0.87 for TSS (Schmilovitch *et al.*, 1995).

Lammertyn *et al.* (2000) contributed to the study of NIR spectroscopy as a non-destructive quality assessment with:

- Comparison between two optical configurations, which can be used to perform NIR spectroscopy measurements. It was concluded that the bifurcated optical was only marginally better than $0^o/45^o$ optical configuration. The light in the bifurcated optical configuration is guided to the sample by source fibres. The source and detector fibres are situated randomly in the head of the bifurcated cable, there is a contact between sample skin and fibres, and this contact has an advantage of higher light intensity than the non-contact source in other configuration. However, the $0^o/45^o$ configuration is the best choice for commercial applications; due to its low cost, the possibility to measure without contact and the only slightly less satisfactory results compared to bifurcated cable.
- A NIR spectrum measured with a $0^o/45^o$ configuration can provide information about the state of the fruit flesh. The background influences the spectrum of the skin and the transmission coefficient differs from zero. The proportion of the skin reflectance to the transmission coefficient is an indicator for the amount of information coming from the background compared to that coming form the skin. It was found that the background information can be found in a NIR spectrum and the amount of information from background exceeds the amount of information from the skin; and
- The light penetration depth for each wavelength in the range from 500-1900 nm in Jonagold apple fruit tissue was calculated. It was concluded that penetration depth is wavelength dependant: up to 4 mm in the 700-900 nm range and between 2-3 mm in the 900-1900 nm range. These values correspond with those obtained by

other researchers, who found that a light penetration depth is 5.5 mm in the range of 500-800 nm for Jonagold apples.

Schaare and Fraser (2000) made a study to compare the relative accuracy of three modes (reflectance, transmission and interactance)[5] of visible-near infrared spectroscopic measurement, for estimating SSC, density and flesh hue of kiwifruit, cv. '*Actinidia chinensis*'. Where:

- Reflectance[6]: is the easiest to obtain since they require no contact with the fruit and light levels are relatively high. Nevertheless, the calibrations may be susceptible to variations in superficial or surface properties of the fruit;
- Transmission: may be also made without contacting the fruit and may be less susceptible to surface properties and better for detecting internal disorders than reflectance mode measurements; and
- Interactance: has a general characteristic intermediate between reflectance and transmission spectra. But obtaining a light seal may be problematic at the high conveyor speeds used in modern fruit grading systems.

It was concluded that good calibrations were obtained in every case, supporting the use of NIR spectroscopy for the rapid and non-destructive evaluation of fruit internal qualities. According to the authors, the most accurate results, which had the lowest SEP, were obtained using interactance mode, followed by transmission mode, and in general reflectance was least accurate. Also, it was found that PLS is the most robust algorithm of those tested for generation calibration models.

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[5] - Optical Density (OD) = $\log_{10} (I_1/I_2)$, where:

$I_1$: The incident radiant energy; and

$I_2$: The radiant energy transmitted through the sample.

- Transmittance (T) is loosely defined as: $T= I_2/I_1$; and
- Absorbance (A)= $\log_{10} (1/T)= \log_{10} (I_1/I_2)$, which is identical to optical density (Chen, 1978).

[6] Reflectance (R): spectral reflectance is generally measured to compare total radiation reflected from the sample with a reflectance from a white surface (e.g. a slab of $BaSO_4$). Reflectance is expressed in percent of the reflectance to the reference (Chen, 1978).

Chen (1978) stated that reflectance is generally easier to use for quality evaluation of agricultural products due to:

1. Its relative high intensity: Since reflectance in the visible and infrared regions ranges up to 80% of the incident energy; and
2. Reflectance measurement is not adversely affected by low-intensity background light.

Different scientists discussed the issue of peeling the commodity before measuring the spectra. Lammertyn *et al.* (2000) stated that the background information can be found in a NIR spectrum and the amount of the information from background exceeds the amount of information from the skin. This indicates that taking spectra of a commodity without peeling is quite acceptable. Krivoshiev *et al.* (2000) stated that if a given product is usually consumed after peeling (in fresh or processed state), it means that the instrumental quality evaluation should be performed on peeled specimens. In this way, the instrumental data would be in best conformity with consumers sensory evaluation. The prediction of the spectrum of the peeled fruit by measuring the whole fruit spectrum is a goal to eliminate the participation of the peel without actual removal.

Krivoshiev *et al.* (2000) developed a method called 'V (virtual)-Method', for elimination of the distorting influence of the skin in measurement of fruit and vegetable transmittance in VIS/NIR regions. This method gives a precise measurement of the flesh spectral transmittance without their destruction, which gives a better identification of the internal quality of fruit and vegetable products. This method was experimentally proved on potatoes within the range of 600-1100 nm.

One of the applications of NIR spectroscopy is for classification of fruits or their products. NIR was used for classification and analysis of citrus oils (Steruer *et al.,* 2001). Also, it was used in a combination with non-destructive impact method for classification of woolly peaches 'mealiness in other fruits' (Ortiz *et al.,*2001). Classification of fruits according to their SSC is possible and recently implemented. Bellon and Sevila (1993) found that it was possible to use NIR for sorting apples, according to their sugar content, into three categories of maturity with 83% of performance. In Japan, there are a number of NIR systems in commercial operation

for the on-line grading of fruit according to sweetness (McGlone and Kawano, 1998). To our knowledge, there are no literatures which discuss using NIR technique for classification or sensing fruits according to their taste or variety.

# 3. Destructive techniques for taste sensing: taste sensor (electronic tongue) & electronic nose

*This chapter presents briefly the destructive method for taste sensing. It presents the work done in the field of electronic tongue and electronic nose.*

In biological taste, the biological membrane of gustatory cells in taste buds on the tongue receives substance producing taste. Information on taste substances is transduced into an electric signal, which is transmitted along the nerve fiber to the brain, where the taste is distinguished (Toko, 2000).

Many methods (concepts) related to the sense of taste have been developed. All of these methods are destructive methods for commodities, since they are for liquid and juice analysis, and most of them are used for analytical chemistry. For these concepts the terms ’taste sensor’ or ‘electronic tongue’ have been coined. Winquist *et al.* (1997) stated some of these methods:

1. An electronic tongue based on a number of chalcogenide glass electrodes, combined with a pattern recognition routine for measurements of metal ions in river water.
2. A more complex sensor composition consisting of glass electrodes and poly vinyl chloride membranes for analysis of beverages.
3. A light addressable potentiometric sensor (LDPS) with artificial lipid membranes as ion selective materials.
4. A taste system based on a fibre optic sensor array using potential sensitive dyes on the surface photo voltage technique applied to Langmuir-Blodgett films.
5. Also, Kiyoshi Toko in Japan has developed a taste sensor based on lipid/polymer membranes on a multi channel electrode; this concept has been commercialized and has proven useful for various applications. A brief explanation of this taste sensor will be mentioned later.

A common feature of these electronic tongues is that the sensing principle is based only on potentiometry, the charging of a membrane being measured. This will limit the range of detectable compound to charged species and will put high demands on the electronics and measurement set-up according to Winquist *et al.* (1997).

6. Winquist *et al.* (1997) developed an electronic tongue based on pulse voltammetry combined with multivariate methods for classification purposes. This sensor was able to classify various fruit drinks and milk, and also able to follow some aging processes.

The electronic nose consists of an array of gas sensors with different selectivity patterns, a signal collecting unit and pattern recognition software applied via a computer. Its principle is based on that a large number of different compounds contributing to define a measured smell, the chemical sensor array to the electronic nose, then provides a pattern output that represents a combination of all the components. The pattern output is given by the selectivities of the various sensors (Winquist *et al.*, 1999).

Di Natale *et al.* (2000) made a combination of electronic nose and electronic tongue to improve the classification of clinic and food samples. They had illustrated a combined approach based on a multi sensor system, to get chemical information from liquid samples through the analysis of the solution and its headspace. Sensors operating in liquid (electronic tongue) and in the headspace (electronic nose) are based on the same sensitive material: the metalloporphyrins. This gives the opportunity of a certain uniformity of interaction experiments in the fields of clinical and food analysis, respectively. The combined system has been shown a net increase of information and classification performances.

Wine flavor was successfully discriminated using the taste sensor and the electronic nose that utilizes conducting polymers (Toko, 2000).

Winquist *et al.* (1999) stated that both the electronic tongue (based on pulsed volammetry for the taste analysis of liquids) and electronic nose alone are able to discriminate reasonably between experimental samples, but the combination of the methods only to a certain limit can improve the classification properties.

Toko K. (1996) developed a taste sensor, which has a new concept of global sensitivity, composed of several kinds of lipid/polymer membranes for transforming

information of taste substances into electric signals, which are analyzed by a computer. According to Toko, the taste is comprised of five basic qualities:

- Sweetness: due to sucrose, glucose, etc.;
- Saltiness: produced mainly by NaCl;
- Sourness: produced by hydrogen ion of HCl, acetic acid , citric acid, etc;
- Bitterness: produced by quinine, caffeine and $MgCl_2$; and
- 'Umani'[7] taste: produced by monosodium glutamate (MSG) contained in seaweeds, disodium inosinate (IMP) in meat and fish and disodium guanylate (GMP) in mushrooms.

The taste sensor is essentially an intelligent sensor to reproduce the taste sense, which is a complex, comprehensive sense of humans. What is important in recognition of taste is the transformation of molecular information contained in interactions with biological membranes into several kinds of groups, i.e. taste intensities and qualities and not discrimination of minute difference in molecular structures. Typically five primary taste substances: HCl (sour), NaCl (salty), quinine (bitter), sucrose (sweet) and MSG (umami). The patterns of substances producing different taste qualities are very different, and hence each taste can be easily discriminated. The taste sensor has similar response patterns to the same group of tastes, as examples of sour substances HCl, citric acid and acetic acid show similar response pattern. Umani substances, MSG, IMP and GMP show similar patterns also. Therefore, it can be concluded that this taste sensor can respond to taste in itself, as can be understood from the fact that taste interactions such as the suppression effect, which appears between sweet and bitter substances, can be well reproduced. Amino acids can be classified into several groups according to their own tastes with sensor outputs. Taste sensor was used for testing the taste of coffee, beer, vegetables (after crushing them) and mineral water.

Chibvongodze (1999), who belongs to Prof. Toko's laboratory in Japan, used NIR to study the effect of taste substances on lipids. In that experiment, both NIR (to measure food constituents using transmittance or reflectance spectra) and lipid membrane taste sensor (to measure basic tastes using the technique of electric potential change) were

[7] The Japanese term for implying deliciousness.

used. Grouping foodstuffs according to their taste qualities was achieved in that experiment.

Fujiwara and Honjo (1996) stated that NIR method could be used to determine total sugar content and Brix value in strawberry juice with sufficient accuracy without control of the sample temperature.

# 4. Identification of the problem, objectives and limitations

*This chapter outlines the problem analysis, research justification, hypothesis, objectives and limitations of the research.*

## 4.1. Problem analysis

At present time, the consumption, marketing and grading of fruits are based on their external aspects. Fruits are stored and marketed visually, manually or automatically on the basis of size, color and surface defects. However, internal attributes like dry matter content, total soluble solids contents (refractive index), juice acidity, firmness, etc., are important. Most instrumental techniques to measure these properties are destructive, and involve a considerable amount of manual work.

In recent years, research has been focused on the development of non-destructive measurement techniques for quality attributes of fruits (mainly: apples) and vegetables such as pH, sugar content and firmness. NIR spectroscopy is one of such techniques. The advantages and major disadvantages of this technique are (Lammertyn *et al.*, 1998; Lammertyn *et al.*, 2000):

- Advantages:
  - Its fast execution;
  - More than one parameter may be estimated at the same time (by using multivariate data analysis technique);
  - Simplified sample preparation;
  - Ease of implementation in process control and grading system; and
  - Lack of chemical pollution.
- Major disadvantages:
  - NIR spectrum is not easy to interpret, since most models are black box models;
  - The equipment is expensive; and
  - New calibration curve is needed for each variety to obtain good results.

Despite these disadvantages, NIR spectroscopy is the most appropriate technique in terms of speed of assessment and cost at the present time (Walsh *et al.*, 2000). In

Japan, there are a number of NIR systems in commercial operation for the on-line grading of fruit according to sweetness (McGlone and Kawano, 1998).

There were many contributions using NIR spectroscopy in the field of non-destructive quality assessing like pH, sugar content, firmness, texture parameters, optimal picking date, light penetration of NIR in fruit and bruises (Lammertyn *et al.*, 2000).

Taste is also an important internal quality parameter of agricultural commodities, an issue not often discussed in the literature. Blanke (1996) stated that fruit's taste is the major asset of fruit quality. This study is addressing the feasibility of using NIR spectroscopy for detecting taste of fruits, based on known NIR ability to predict SSC, acidity and chemicals components.

A non-destructive NIR technique (reflectance mode) for sensing taste of fruits and vegetables may open a wide range for an automatic NIR taste sensor, which will be greatly appreciated among package storage houses, and great store markets for grading fruits according to their taste quality. Since, in practice, apples (for example) are sold in batch and the internal quality of the whole batch is estimated by the average of the lab values of sample sub set. With this method (NIR technology) all apples could be controlled (Moons *et al.*, 2000).

## 4.2. Hypothesis

The hypothesis of this study is that NIR technique can detect the taste of fruits and vegetables.

## 4.3. Objectives

The objectives of this study is to verify the hypothesis through:

1. Predicting some internal quality parameters of fruit (like SSC, acidity) using NIR spectroscopy;
2. Classification of two different varieties of the same fruit based on their NIR reflectance;

3. Classification of two different varieties of the same fruit when having the same SSC/acidity values based on their NIR reflectance; and
4. Using multivariate analysis for analyzing the data.

Taste of any fruit is considered to be composed from SSC, acidity and characteristic taste parameters of the fruit (distinguished chemicals). The basis for this work is that if it is possible, using NIR technology, to classify two different varieties (of the same commodity) having the same SSC/acidity values, then NIR can detect the characteristic taste parameters in both varieties.

## 4.4. The limitation of NIR

The general limitations of using NIR are (Kupferman, 1997):

1. The chemical constituents: NIR can detect only chemical compounds which contain CH, OH or NH groups, but as the main content of the fruit is water, the differentiation between water and chemicals constituent of interest can be difficult; and
2. Physical problem associated with light transmitance and reflectance through the fruit: the orientation of the fruit to the light beam in the sorting machine may be also a problem.

## 4.5. The limitation of the research

The limitations of this research are:

1. For measuring the internal quality of fruit and vegetable in reflectance mode, the calibration may be susceptible to variations in superficial or surface of the fruit (Schaare and Fraser, 2000). In this research's experiments, a holder was designed to direct the NIR light in a 45 degree angle to the fruit (to avoid specular reflectance). And for each fruit, three reflection spectra were taken at three equidistant positions around the equator in order to obtain a good estimation of the whole fruit and to eliminate the spatial variability; and
2. Applying automatic sorting or quality control in agricultural is not as straightforward as applying them in other industries such as the electronic and

automotive. There are two main differences. Firstly, the working agricultural environment is highly variable (weather, soil, etc). Secondly, agricultural products are highly variable due to their inherent morphological diversity (Blackmore and Steinhouse, 1993).

# 5. Methodology

*This chapter describes the methodology followed in this study. It gives a clear description of the materials, procedure, theory and analysis during the research.*

## 5.1. Materials

### 5.1.1. The instrument

The equipment that was used in the experiment is an OEM (Original Equipment Manufacture) device. It is tec5 company multi operating spectrometer system.

The spectrometer system consists of two parts (see Fig. 5):

1. Light source; and
2. Spectrometer optical components.

For more explanation of these parts:

1. The light source consisted of a 12V/100W tungsten halogen lamp. It is controlled by a photodiode sensor. The halogen lamp has the following advantages (Nielsen, 2001):
   - The best light source for NIR light range;
   - Can be used in both visible and NIR range;
   - Relatively less expensive than other lamps types;
   - Light produced gives smooth wavelength curves;
   - Light produced has high quality; and
   - Light produced has high stability.
2. The spectrometer optical system is based on:
   2.1. A Zeiss monolithic miniature spectrometer (MMS 1) NIR enhanced, which consists of a body made of UBK 7 glass with aberration corrected grating. The Zeiss MMS 1 NIR enhanced is the sensor. The detection range of this sensor is 306-1132 nm. The advantages of this type of sensor are (Zeiss company, 1999):
      - Robust and thermally stable;
      - Compact, permanently aligned;
      - Use for diverse measuring tasks;
      - High light sensitivity; and

- Small.

2.2. A fiber cross section converter (circular light shape to line shape) as optical entrance; and

2.3. A Hamamatsu (S4781, 256 pixels) photo diode array (PDA) as a detector. Order sorting filters are applied during manufacture to different regions of the array to eliminate detection of second order spectra over this wide wavelength range (306-1132 nm). A 15-bit analogue to digital conversion device was used, under the control of tec5 software. Diode arrays have the following advantages over CCDs (Zeiss company, 1995):

- ♦ Large dynamic range (for non-cooled devices);
- ♦ Better ultra violet (UV) sensitivity;
- ♦ No trailing effect;
- ♦ Intensity- independent noise; and
- ♦ Minimum cross-talk.

Both of fiber cross section converter and PDA are fixed to the glass body of MMS 1 NIR enhanced Zeiss sensor (Fig. 4).

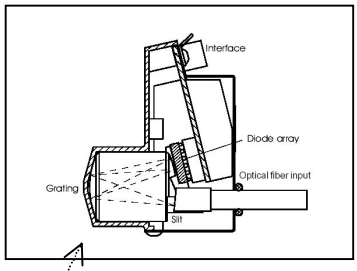


*Fig. 4. Zeiss MMS 1 NIR enhanced sensor module.*
Source: Zeiss company (1999).

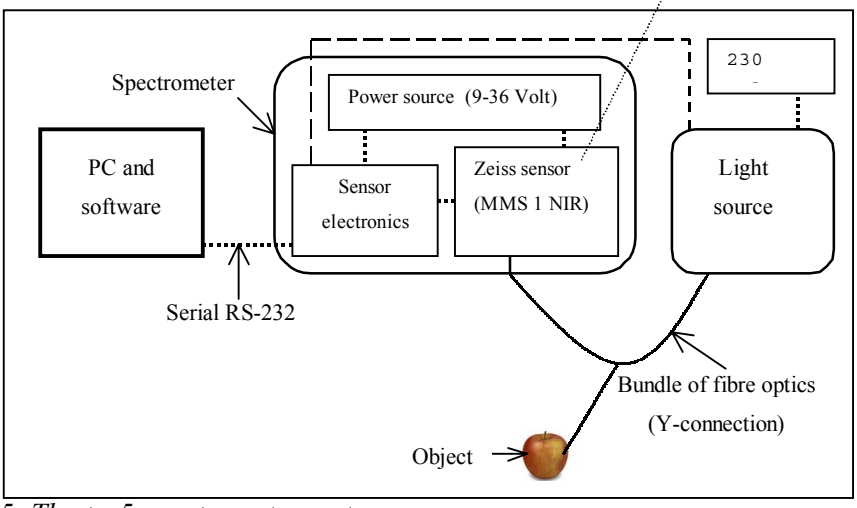


*Fig. 5. The tec5 spectrometer system.*

### 5.1.2. Fruits (plums & apples)

- Plums:

  One experiment was carried out on two varieties of plums, Reine Claude (*Prunus domistica*) and Blackamber (*Prunus silicina*). Plums were obtained from a local supplier. Eighty plums of each variety were used.

- Apples:

Two separated experiments on apples (*Malus domestica*) have been carried out:

*1st experiment:* One hundred apples of each variety. Golden Delicious and Jonagold were used; and

*2nd experiment:* One hundred apples of each variety. Aroma and Elstar were used. Apples were obtained from KVL's orchard research farm. After being in cold store, apples were kept at the room temperature for 24 hours for equilibration before the experiments. These four apple varieties are among the most preferred apples in Denmark (Hoffmann, 2001).

## 5.2. Methods

### 5.2.1. Reflectance measurements

A scanning Zeiss MMS1 NIR enhanced spectrometer was used to collect reflectance readings over a wavelength range of 700-1100 nm in 2 nm increments, yielding 200 values per spectrum. For each fruit, three reflection spectra were taken at three equidistant positions around the equator in order to eliminate the spatial variability. A plate made of $BaSO_4$ was used as a reference spectrum. Each reflectance spectrum used in analysis was an average of the three spectra obtained for each fruit. The light source consisted of 12V/100W tungsten halogen lamp. The light passes through a bundle of optical fibres to the fruit, and reflected light is transferred to a photo diode array (PDA) detector through another bundle of fibre optic. A holder was designed to support fruits and to direct the light in a 45 degree angle to fruits (to avoid specular reflectance), and to maintain a distance of 1 cm between the probe and the plums. The spectrometer has a very good stability versus time and temperature. The integration

time (time needed for a spectrum to be acquired) was 181 milli second (ms) for plums and 161 ms for apples.

In this study, the commodities were not peeled before reflectance measurement, based on Lammartyn *et al.* (2000) conclusion, which stated that the background information can be found in a NIR spectrum and the amount of the information from background exceeds the amount of information from the skin. This indicates that taking spectra of a commodity without peeling is quite reasonable.

### 5.2.2. Chemical and physical analysis

- SSC: A digital refractometer (RFM 90-Struers) was used to measure SSC of fruit juice. Each reading was an average of five times, and two trials were made for each fruit (the SSC results were an average of 10 times). The SSC was expressed in Brix.
- Acidity: A 719 S Titrino was used for measuring acidity. Fruit juice acidity was obtained using a NaOH 0.1 N. Results were expressed in grams of NaOH needed to titrate 100 grams of fruit juice until pH's solution reached 8.1.
- Firmness (only for Golden Delicious & Jonagold experiment): Bosch penetrometer (model FT 327) was used to measure the firmness. Two measures have been taken on each fruit at opposite sides, at the middle point of each side, after removing 0.7-1.1 cm diameter disk of peel. The firmness was expressed in $kg/cm^2$.

### 5.2.3. Procedure

Three separated experiments were carried out, one for plums and two for apples. For each experiment:

1. Two varieties of the same fruit were used ;
2. Fruits were stored in the lab room for 24 hours for equilibration before the experiment;
3. Each fruit was labeled with two numbers. The first no. was the variety abbreviation, and the second no. was the sequence no. (i.e. B 1-80 and R 1-80);

4. Spectrum for each fruit in 3 equidistant positions along the equator was taken;
5. Firmness (only for Golden Delicious and Jonagold experiment) was taken by Bosch penetrometer;
6. Fruit's juice was prepared by using a mixer;
7. SSC of fruit's juice were measured by refrectometer;
8. Acidity of fruit's juice were measured by A 719 S Titrino; and
9. The spectra, chemical and physical data were collected to be analyzed.

### 5.2.4. Theory

- Fruit taste as the major asset of fruit quality is dominated by the surgar:acid ratio (Blanke, 1996). Groups of fruits (plums or apples) from both varieties, which have the same ratio of SSC and acidity, were gathered for classification. Having the same values of SSC/acidity means that both components (sugar and acidity) are eliminated leaving only the characteristic taste parameters of the variety (distinguished chemicals) to be detected. Investigating the possibility of classifying these groups will open a wide range for studying other taste parameters.

- NIR spectroscopy is an indirect measurement technique for quality parameters. This means that specific calibration models have to be calculated beforehand. Figure 6 shows the general modeling process in two steps. In the first step: the model is calculated using the NIR spectra and the reference measurements. In the second step: the calculated model is used to predict the reference parameter based upon measured NIR spectra. This study is addressing the possibility of NIR to detect taste, in further stages, it may be possible to predict each taste parameter (as it is possible to predict SSC in nowadays) after identifying it. In this study, PLS method was used for modeling, since PLS models don't include the latent variables that are not important to describe the variance of desired parameters, which means that PLS models will have the lowest number of variables (Lammertyn *et al.*, 1998).

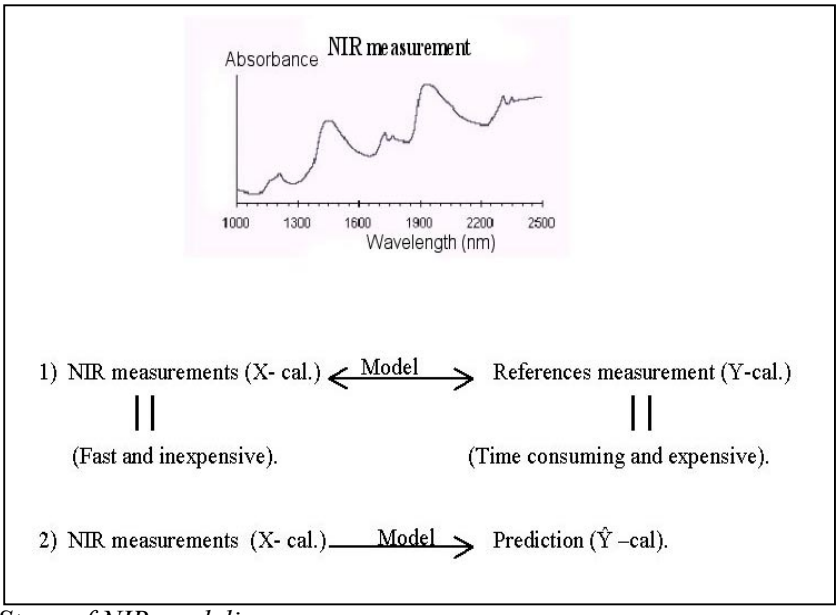


*Fig. 6: Steps of NIR modeling process.*

### 5.2.5. Data analysis

The calculations were carried out using 'Unscrambler' v. 7.5 (CAMO, ASA, Oslo, Norway), a statistical software package for multivariate analysis. Matlab R.12 (The Math Works Inc., Natick, MA) was used as a bridge program between the spectrometer outputs and Unscrabmbler to transfer the reflectance data to be analyzed.

# 6. Results, Discussion and Conclusion

In this chapter, two attached articles, which have been submitted to two different international journals:

- International Agrophysics Journal; and
- Journal of Agricultural Engineering Research.

will give a comprehensive idea of the study results, discussion and conclusion.

# SENSING TASTE OF FRUITS USING NEAR INFRARED TECHNOLOGY

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## Abstract

This project concerns the feasibility of using near infrared (NIR) technology for sensing taste of fruits. The aim is to improve a non-destructive method related to development of taste components (other than sugar content and acidity) for detecting characteristic taste parameters in different commodities. Such sensors can be used online in fruit grading, according to their taste quality, in warehouses and public fruit markets. In this experiment, a NIR spectrometer with photo diode array (PDA) detector, was able to classify two varieties of plums (Reine Claude and Blackamber) which had the same ratio of soluble solid contents (SSC) and acidity. Non-destructive classification was based on optical reflectance in NIR range (700-1100 nm). Both of Reine Claude and Blackamber were correctly classified in 92.8% of the cases at 5% significant level, which indicates that NIR detects the taste of different varieties.

*Keywords*: NIR, quality, non-destructive, taste, classification.

## 1. Introduction

In recent years, research has focused on the development of non-destructive techniques for measuring quality parameters of different commodities. NIR spectroscopy is one of these techniques. NIR spectroscopy is uniquely qualified for analysis in food and related industries, through its interaction with the organic molecular material of foodstuffs. Most food is organic, containing C-H, C-O-H and C-N-H, etc. These bonds interact in a measurable way with the NIR portion of the spectrum. NIR light is energetic enough to bring atoms within a molecule in vibration relative to each other. These interactions occur at the speed of light providing extremely rapid information gathering capabilities. NIR range is the only part of the electromagnetic spectrum in which this particular measurable interaction occurs. NIR creates a faster, safer work environment and does not require chemicals (Shadow, 1997; Timmermans, 2000).

There were many contributions in the field of assessing pH, sugar content, firmness, texture parameters, optimal picking date, light penetration of NIR in fruit and bruises using NIR spectroscopy (Lammertyn *et al*., 2000).

NIR ranges were different from one contribution to another. In this experiment, wavelengths between 700-1100 nm were used. NIR in this range is promising and more useful for intact foods due to the following facts (Carlini *et al.*, 2000; McGlone and Kawano, 1998; Walsh *et al*., 2000):

1. Radiation can penetrate much further in fruit of many different species;
2. The corresponding instrumentation has low cost, suits to process control and is portable enough for in situ field measurements;
3. The bands are ascribed to the third and forth overtones of O-H and C-H stretching modes and are expected to be separated due to anharmonicity;
4. Lower absorbance at these wavelengths allows for transmission optics; and
5. Water absorbance peaks are less strong and broad and the risk to mask spectral information correlated to low concentration constituents is low.

Optical measurements can be done in different modes: transmittance, absorbance and reflectance. Chen (1978) stated that reflectance is generally easier to use for quality evaluation of agricultural products due to:

1. Its relative high intensity: Since reflectance in the visible and infrared regions ranges up to 80% of the incident energy; and
2. Reflectance measurement is not adversely affected by low-intensity background light.

Taste is an important internal quality of a commodity, an issue not often discussed in the literature. Taste of any fruit is considered to be composed from SSC, acidity and characteristic taste parameters of the fruit (distinguished chemicals). The basis for this work is that if it is possible, using NIR technology, to classify two different varieties (of the same commodity) having the same SSC/acidity values, then NIR can detect the characteristic taste parameters in both varieties.

## 2. Methodology

### 2.1. Fruits

Experiment was carried out on two varieties of plums, Reine Claude (*Prunus domistica*) and Blackamber (*Prunus silicina*). Plums were obtained from a local supplier. Eighty plums of each variety were used.

## 2.2. Reflectance measurements

A scanning Zeiss MMS1 NIR enhanced spectrometer was used to collect reflectance readings over a wavelength range of 700-1100 nm in 2 nm increments, yielding 200 values per spectrum. For each plum, three reflection spectra were taken at three equidestant positions around the equator in order to eliminate the spatial variability. A plate made of $BaSO_4$ was used as a reference spectrum. Each reflectance spectrum used in analysis was an average of the three spectra obtained for each plum. The light source consisted of 12V/100W tungsten halogen lamp. The light passed through a bundle of optical fibres to the fruit, and reflected light is transferred to a photo diode array (PDA) detector through another bundle of fibre optic. A holder was designed to support plums and to direct the light in a 45 degree angle to the plums (to avoid specular reflectance), and to maintain a distance of 1 cm between the probe and the plums. The integration time (time needed for a spectrum to be acquired) was 181 milli second (ms).

## 2.3. Chemical analysis

- Soluble solid contents (SSC): A digital refractometer (RFM 90-Struers) was used to measure SSC of plum juice. Each reading was an average of five times, and two trials were made for each plum (the SSC results were an average of ten times). The SSC was expressed in Brix.
- Acidity: A 719 S Titrino was used for measuring acidity. Plum juice acidity was obtained using a NaOH 0.1 N. Results were expressed in grams of NaOH needed to titrate 100 grams of plums juice until pH's solution reached 8.1.

## 2.4. Theory

Fruit taste as the major asset of fruit quality is dominated by the surgar:acid ratio (Blanke, 1996). Groups of plums, which have the same SSC/acidity values, were gathered for classification. Having the same ratio of SSC and acidity means that both components (sugar and acidity) are eliminated leaving only the characteristic taste parameters of the variety to be detected. Investigating the possibility of classifying these groups will open a wide range for studying other characteristic taste parameters.

## 3. Results

- The calculations were carried out using 'Unscrambler' v. 7.5 (CAMO, ASA, Oslo, Norway), a statistical software package for multivariate analysis. Matlab R.12 (The Math Works Inc., Natick, MA) was used as a bridge program between the spectrometer outputs and Unscrambler to transfer the reflectance data to be analyzed.
- The averaged values of SSC and acidity for each plums variety is tabulated in Table 1.

*Table 1. Chemical reference values of Reine Claude and Blackamber plums.*

| Variety | SSC (Brix) | | | | Acidity (g/100g) | | | |
|---|---|---|---|---|---|---|---|---|
| | *Average* | *SDev** | *CV** | *Range* | *Average* | *SDev* | *CV* | *Range* |
| Reine Claude | 11.54 | 2.21 | 0.19 | 7.5-16.5 | 1.05 | 0.43 | 0.41 | 0.1-1.97 |
| Blackamber | 8.55 | 1.77 | 0.21 | 4.5-12.3 | 1.06 | 0.20 | 0.19 | 0.53-1.57 |

**SDev: Standard Deviation.*

**CV: Coefficient of Variation.*

- SSC between two varieties was significantly different, while acidity was insignificant between two varieties at 5% significant level. The correlation between acidity and SSC was very low.
- All the analysis (modelling and classification) was based on full multiplicative scatter correction (MSC) transformed data. It was found that full MSC preprocessing technique describes the data better than the raw data itself or first and second derivative preprocessing techniques. MSC pre-processing technique yielded the lowest root mean square error of prediction (RMSEP) and distinguished groups (two varieties) are very clear along the first principal components (PCs). This technique corrects the additive and multiplicative effects in the spectra and improves the predictive ability (Mobley *et al.,* 1996)
- For calibration 100 samples have been used, about 60 samples were used for validation.
- In the reflectance spectra scores plot (Fig. 1) of all plum samples (from both varieties), the first principal component (PC) describes 68% of the variation between all samples.

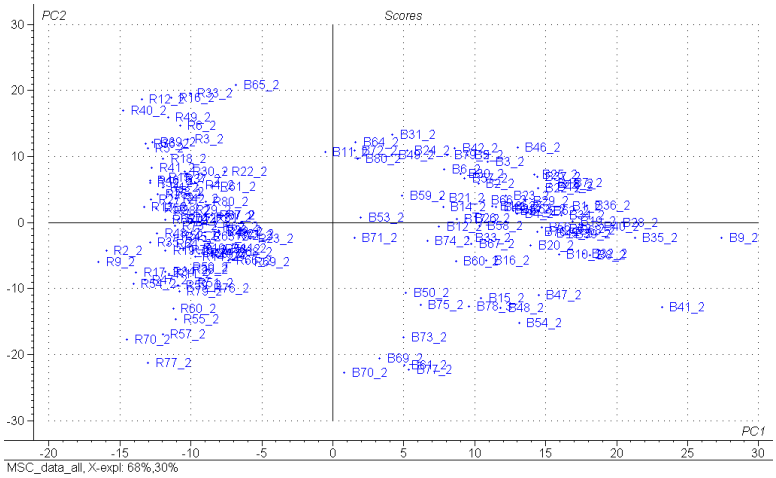


*Fig. 1. Reflectance spectra scores (MSC pre-processed) plot of all plum samples. The first principal component (variety) describes 68% of the variation between samples*

- Partial least square (PLS-1) method was used for modelling SSC for both varieties. SSC has a validation correlation of 79.9% and a RMSEP of 1.56 with four PCs. Figure 2 shows the PLS model for SSC.

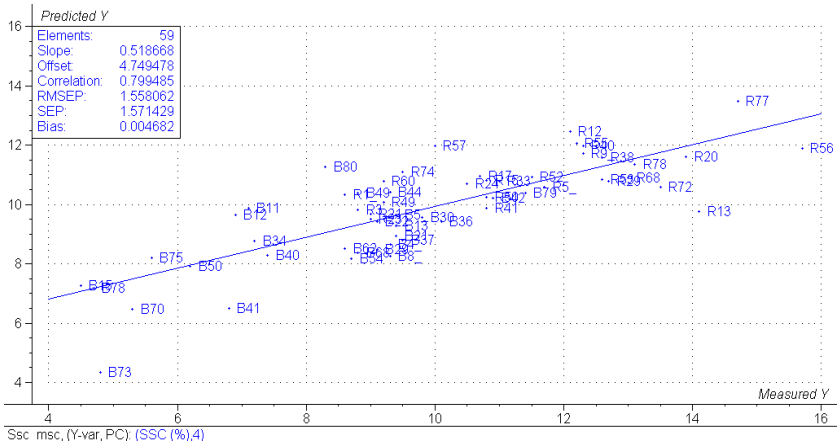


*Fig. 2. PLS model for SSC of all plum samples.*

- The acidity modelling was not satisfactory. The correlation was very low.
- The most important range of NIR for modeling, which has the highest loading, was 700-950 nm.
- Soft independent modelling of class analogies (SIMCA) classification method was used to classify all plum samples (160 samples) according to their MSC pre-processed reflectance spectra. The train set contained 50 samples and test set contained 30 samples for each variety. A classification is considered as an error when the sample does not belong to any of the models. Reine Claude and Blackamber were correctly classified in 90% and 96.6% of the cases respectively at 5% significant level. Coomans plot (objects to model distance) in Fig. 3 shows a very clear distinguished groups of both varieties.

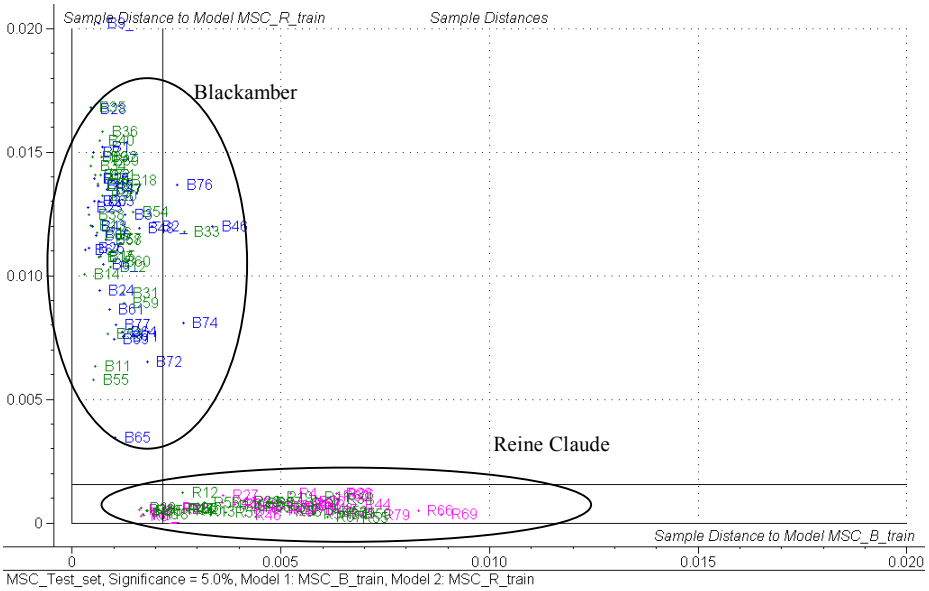


*Fig. 3. Coomans plot for all Blackamber and Reine Claude samples (train and test sets), at 5% significant level.*

- For the groups having the same values of SSC/acidity within ±5% (approximately 30 samples from each variety), the first PC explains 90% of the variation between these samples (Fig. 4 and Fig. 5). A clear distinguished groups (two varieties) along the first principal component can be seen in Fig. 4.

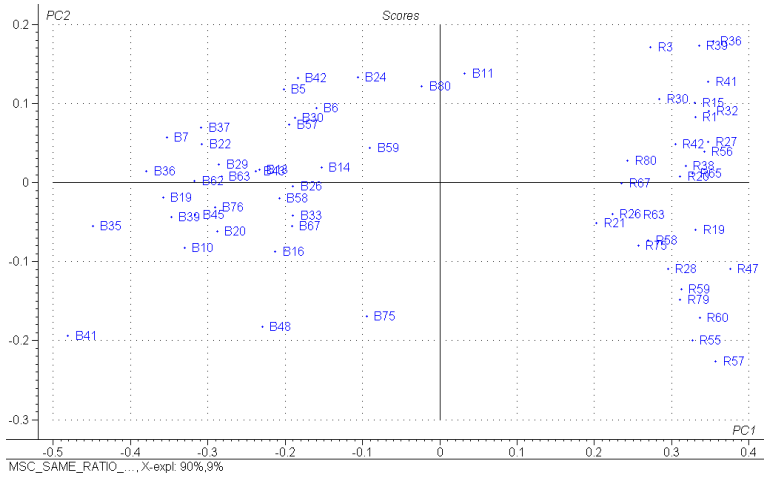


*Fig. 4. Scores plot of the reflectance spectra of plum samples, which have the same ratio of SSC and acidity (approximately 30 samples from each variety). The first principal component explains 90% of the variation between samples.*

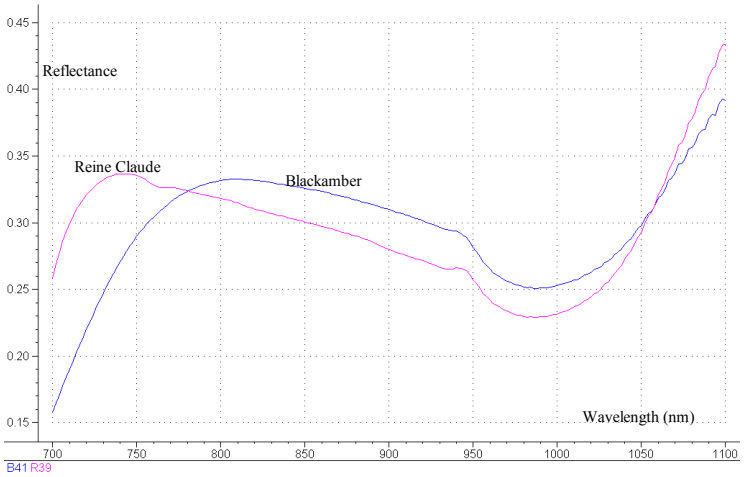


*Fig. 5. Averaged reflectance spectra (MSC pre-processed) of plum samples having the same ratio of SSC and acidity.*

- Samples having the same values of SSC/acidity were 63 plums from both varieties. SIMCA was used to classify them. Reflectance spectra of 35 samples from both varieties were used in the training set. The reflectance spectra of the rest (28 samples) were used in the test set. Results at 5% significant level are shown in Table 2. Coomans plot in Fig. 6 shows a very clear distinguished groups of both varieties.

- *Table 2: Classification result (SIMCA method) of NIR reflectance spectra for two plum varieties having the same values of SSC/acidity.*

| *Variety* | *Reine Claude* | *Blackamber* | *Error* |
|---|---|---|---|
| Reine Claude | 92.8%% | 0% | 7.2% |
| Blackamber | 0% | 92.8% | 7.2% |

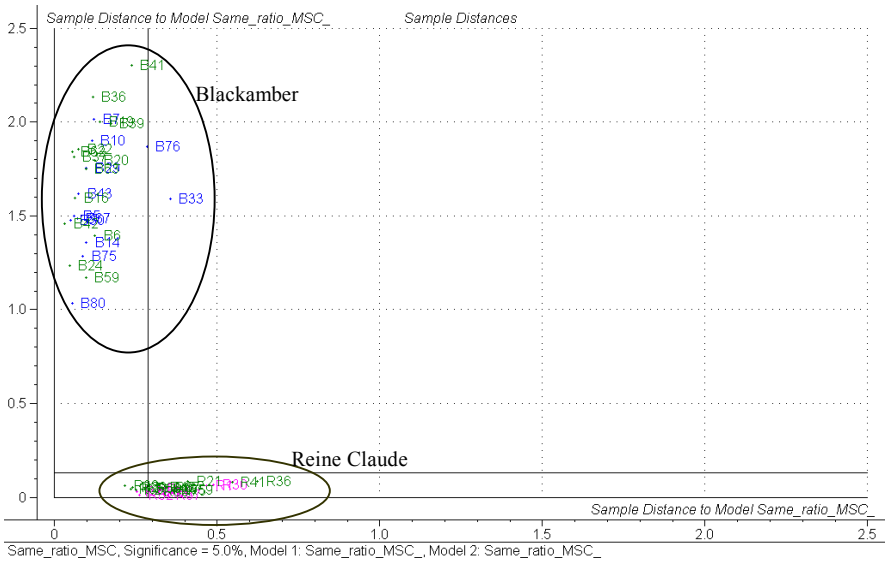


*Fig. 6. Coomans plot for all Blackamber and Reine Claude samples which have the same ratio of SSC and acidity, at 5% significant level*

- The most important ranges of NIR, for classification between groups having the same values of SSC/acidity, were 715-740 nm and 820-850 nm.

## 4. Discussion

- Considering all plum samples, the first principal component explains 68% of the variation between samples (Fig. 1). And when considering the samples having the same values of SSC/acidity, the first principal component explains 90% of the variation between samples (Fig. 3). This first principal component (latent factor) can be interpreted as variety factor, since there is a clearly separated groups (two varieties) along this vector.
- There was a high variation in SSC of both plums' varieties (CV is about 20%). Also, acidity in both varieties had a high variation (CV is bout 30%). This indicates that the samples were not too much homogenous in terms of SSC and acidity aspects. Anyhow, there were samples that had the same SSC/acidity values.

- It was possible to model SSC, with a reasonable correlation. Acidity was difficult to be modeled, so the reflectance spectra do not tell much about acidity. This may be due to limited range of plums acidity and high variation in it.
- The most important range for modeling was about 700-950 nm. The photo diode array has a lower sensitivity for high wavelengths.
- Classification of all plum samples was high with no overlapping between the classification of both varieties.
- Classification accuracy of groups having the same ratio of SSC and acidity was also high with no overlapping between both varieties. Clearly separated groups can be seen in Fig. 6.
- Classification of all plum samples was relatively high even though the first PC just explains 68% of the variation between samples. Reine Claude and Blackamber were correctly classified in 90% and 96.6% of the cases respectively at 5% significant level. When considering classification of samples having the same values of SSC/acidity, the first PC explains 90% of the variation between these samples. Both Reine Claude and Blackamber were correctly classified in 92.8% of the cases at 5% significant level.
- The characteristic taste parameters that distinguish between the two varieties seem to be in the range of 715-740 nm and 820-850 nm, since these ranges have the highest discrimination power. More investigation of the chemicals in these ranges should be done.

## 5. Conclusion

- NIR spectrometer has an ability to classify two varieties of plums, even when they have the same values of SSC/acidity. This result is promising for studying other taste parameters than SSC and acidity, since it indicates that NIR is able to sense taste of fruits.
- Further work using NIR technology will be carried out at The Royal Veterinary and Agricultural University (KVL) on apples and tomatoes, to follow the development of taste components during maturation and to investigate more taste parameters.

## Acknowledgements

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# Using Near Infrared (NIR) Technology for Sensing Apples' Taste

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## Abstract

This project concerns the feasibility of using near infrared (NIR) technology for detecting fruits' taste. The aim is to improve a non-destructive system related to development of taste components (other than sugar content and titrable acidity) for detecting the characteristic taste parameters in different commodities. This system can be used online in fruit grading in warehouses and public fruit markets. The experiments discussed in this paper have been carried out on apples based on the promising results achieved from plums. A NIR spectrometer, with photo diode array (PDA) detector, was used to predict some of the internal quality parameters; i.e. soluble solid contents (SSC), acidity and firmness; and to sense characteristic taste parameters of two different apple varieties (Aroma and Elstar). Non-destructive prediction and classification was based on optical reflectance in NIR range (700-1100 nm). A good correlation between NIR and quality parameters was achieved. Samples having the same ratio of SSC and acidity, were correctly classified in 100% and 85% cases respectively at 10% significant level. Successful classification indicates that NIR technique has a high potential for detecting taste of fruits.

## 1. Introduction

In recent years, research has focused on the development of non-destructive techniques for measuring quality parameters of different commodities. NIR spectroscopy is one of these techniques. NIR spectroscopy is particularly sensitive to the presence of molecules containing C-H, O-H, and N-H groups. These bonds interact in a measurable way in the NIR portion of the spectrum, thus constituents such as starch and sugars (C-H), alcohols, moisture and acids (O-H), and protein (N-H) can be quantified in solids, liquids and slurries. In addition, the analysis of gases is possible. NIR is not a trace analysis technique and is generally used for measuring components that are present at concentrations greater than 0.1%. NIR creates a faster, safer work environment and does not require chemicals. [1]

There were many contributions in the field of assessing pH, sugar content, firmness, texture parameters, optimal picking date, light penetration of NIR in fruit and bruises using NIR spectroscopy. [2]

NIR ranges were different from one contribution to another. In this experiment, wavelengths between 700-1100 nm were used. NIR in this range is promising and more useful for intact foods due to the following facts:[3-5]

1. Radiation can penetrate much further in fruit of many different species;
2. The corresponding instrumentation has low cost, suits to process control and is portable enough for in situ field measurements;
3. The bands are ascribed to the third and forth overtones of O-H and C-H stretching modes and are expected to be separated due to anharmonicity;
4. Lower absorbance at these wavelengths allows for transmission optics; and
5. Water absorbance peaks are less strong and broad and the risk to mask spectral information correlated to low concentration constituents is weak.

Optical measurements can be done in different modes: transmittance, absorbance and reflectance. Chen [6] stated that reflectance is generally easier to use for quality evaluation of agricultural products due to:

1. Its relative high intensity: Since reflectance in the visible and infrared regions ranges up to 80% of the incident energy; and
2. Reflectance measurement is not adversely affected by low-intensity background light.

Taste is an important internal quality of a commodity, an issue not often discussed in the literature. Taste of any fruit' is considered to be composed from SSC, acidity and characteristic taste parameters of the fruit (distinguished chemicals). The basis for this work is that if it is possible, using NIR technology, to classify two different varieties (of the same commodity) having the same SSC/acidity values, then NIR can detect the characteristic taste parameters in both varieties.

The work discussed in this paper was carried out on apples, based on the promising results which have been achieved from plums in AgroTechnology Section at KVL University, to investigate the NIR spectrometer's ability to sense characteristic taste parameters of two plums' varieties. NIR spectroscopy was able to classify Reine Claude and Blackamber, which had the same ratio of SSC and acidity. Both of the varieties were correctly classified in 92.8% of the cases at 5% significant level. This indicates that NIR technology could sense plums' taste.

# 2. Materials and methods

## 2.1. Fruits

Two separated experiments on apples (*Malus domestica*) were carried out. The varieties Golden Delicious, Jonagold, Aroma and Elstar were used. These four apple varieties are among the most popular apples in Denmark.

1st experiment: One hundred apples of each variety. Golden Delicious and Jonagold were used to predict SSC, acidity and firmness. Classification of both varieties was carried out.

2nd experiment: One hundred apples of each variety. Aroma and Elstar were used to predict SSC and acidity. Classification of samples having the same SSC/acidity values was carried out.

Apples were obtained from KVL's orchard research farm. Apples were taken from cold store and kept at room temperature for 24 hours for equilibration before the experiments.

## 2.2. Reflectance measurements

A scanning Zeiss MMS1 NIR enhanced spectrometer was used to collect reflectance readings over a wavelength range of 700-1100 nm in 2 nm increments, yielding 200 values per spectrum. For each apple, three reflection spectra were taken at three equidistant positions around the equator in order to eliminate the spatial variability. A plate made of $BaSO_4$ was used as a reference spectrum. Each reflectance spectrum used in analysis was an average of the three spectra obtained for each apple. The light source consisted of 12V/100W tungsten halogen lamp. The light passed through a bundle of optical fibres to the fruit, and reflected light was transferred to a photo diode array (PDA) detector through another bundle of fibre optic. A holder was designed to support the apples and to direct the light in a 45 degree angle to the apples (to avoid specular reflectance), and to maintain a distance of 1 cm between the probe and the apples. The spectrometer had a very good stability versus time and temperature. The integration time (time needed for a spectrum to be acquired) was 161 ms.

## 2.3. Chemical and physical analysis

- Soluble solid contents (SSC): A digital refractometer (RFM 90-Struers) was used to measure SSC of apple juice. The SSC was expressed in Brix.
- Acidity: A 719 S Titrino was used for measuring acidity. Apple juice acidity was obtained using a NaOH 0.1 N. Results were expressed in grams of NaOH needed to titrate 100 grams of apple juice until pH's solution reached 8.1.

- Firmness (only for Golden Delicious and Jonagold experiment): Bosch penetrometer (model FT 327) was used to measure the firmness. Two measures were taken on each fruit at opposite sides, at the middle point of each side, after removing 0.7-1.1 cm diameter disk of peel. The firmness was expressed in $kg/cm^2$.

## 2.4. Theory

- Fruit taste as the major asset of fruit quality is dominated by the surgar:acid ratio.[7] Groups of apples from two different varieties, which have the same SSC/acidity values, will be gathered for classification. Having the same ratio of SSC and acidity means that both components (sugar and acidity) are eliminated leaving only the characteristic taste parameters of the variety to be detected.

- NIR spectroscopy is an indirect measurement technique for quality parameters. This means that specific calibration models have to be calculated beforehand. The modeling process has two steps. In the first step: the model is calculated using the NIR spectra and the reference measurements. In the second step: the calculated model is used to predict quality parameters based upon measured NIR spectra. This study is addressing the possibility of NIR to detect taste, in further stages, it may be possible to predict each taste parameter (as it is possible to predict SSC in nowadays) after identifying it.

# 3. Results

- The calculations were carried out using 'Unscrambler' v. 7.5 (CAMO, ASA, Oslo, Norway), a statistical software package for multivariate analysis. Matlab R.12 (The Math Works Inc., Natick, MA) was used as a bridge program between the spectrometer outputs and Unscrambler to transfer the reflectance data to be analyzed.

## 3.1. Golden Delicious and Jonagold experiment

- The chemical and physical reference values of 200 apples are tabulated in Table 1.

*Table 1. Chemical and physical reference values of Golden Delicious and Jonagold apples.*

| Variety | SSC (Brix) | | | | Acidity (g/100g) | | | | Firmness ($Kg/cm^2$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | SDev* | CV* | Range | Mean | SDev | CV | Range | Mean | SDev | CV | Range |
| Golden Del. | 12.13 | 0.90 | 7% | 9.20-13.90 | 0.57 | 0.07 | 12% | 0.41-0.78 | 9.52 | 0.76 | 7% | 8.00-12.05 |
| Jonagold | 13.60 | 0.72 | 5% | 12.12-15.65 | 0.83 | 0.08 | 9% | 0.67-1.08 | 10.44 | 0.85 | 8% | 8.80-12.70 |

*SDev: Standard Deviation.

*CV: Coefficient of Variation.

- The SSC, acidity and firmness were significantly different between both varieties at 5% significant level.
- The correlation coefficients between the different parameters of quality are tabulated in Table 2.

*Table 2. The correlation coefficients between the quality parameters.*

| Quality parameter | SSC (Brix) | Acidity (g/100g) | Firmness (Kg/cm$^2$) |
|---|---|---|---|
| SSC (Brix) | ------ | 81.7% | 52.5% |
| Acidity (g/100g) | ------ | ----- | 57.9% |

- For modeling (predicting) each quality parameter by NIR reflectance, partial least square regression (PLS-1) was used. For calibration 130 samples were used. For validation 70 samples were used. It was noticed that full multiplicative scatter correction (MSC) pre-processing technique yielded the best method. It yielded the lowest root mean square error of prediction (RMSEP), the highest validation correlation ($r^2$), the lowest number of principal components (PCs) and the lower difference between the root mean square error of prediction (RMSEP) and calibration (RMSEC).[2] Therefore, MSC was chosen to build quality models. The MSC technique corrects the additive and multiplicative effects in the spectra and improves the predictive ability.[8] The mean reflectance of both varieties is shown in Fig. 1. The result of modeling quality parameters by NIR is tabulated in Table 3. The predicted versus the measured SSC values is shown in Fig. 2.

*Table 3. The calibration results for determination of quality parameters.*

| Quality parameter | RMSEP | $r^2$ | PCs | RMSEC |
|---|---|---|---|---|
| SSC (Brix) | 0.59 | 82.2% | 6 | 0.55 |
| Acidity (g/100g) | 0.07 | 84.3% | 4 | 0.07 |
| Firmness (Kg/cm$^2$) | 0.78 | 58.3% | 6 | 0.71 |

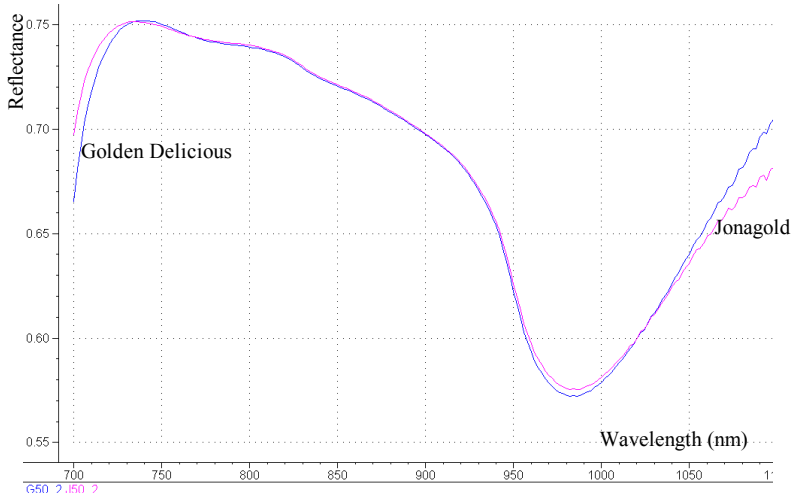


*Fig. 1. Mean reflectance of Golden Delicious and Joangold (MSC pre-processing was used).*

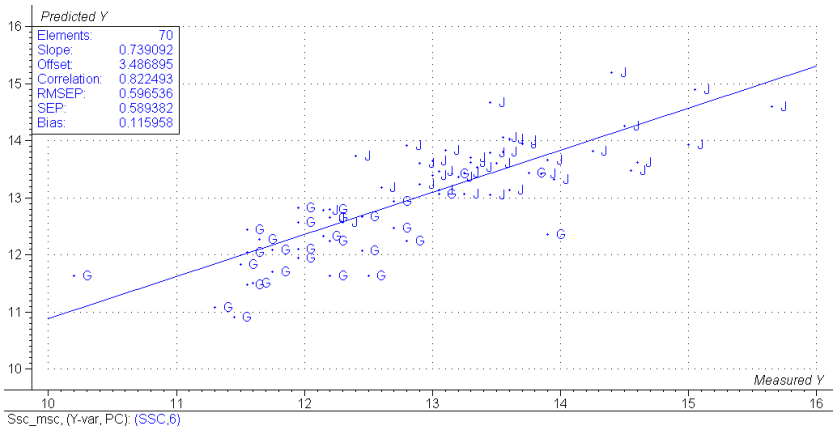


*Fig. 2. The predicted versus the measured SSC values for the validation set of Golden and Jonagold varities.*

- Classification based on the raw data of NIR reflectance of both varieties was carried out using soft independent modelling of class analogies (SIMCA). The raw data was better than any pre-processing techniques to classify apple varieties. The training set contained 70 samples and test set contained 30 samples for each variety. Full cross validation was used for building the principal components models for each variety. The classification percentage result was depending on the SIMCA's classification table and illustrations. A classification is considered an error when the sample does not belong to any of the models. The result of SIMCA classification at 5% significant is tabulated in Table 4. The relative distance versus leverage plot for train set of Golden Delicious is shown in Fig. 3. Some overlapping can be noticed in this figure.

*Table 4. Classification result for Golden Delicious and Jonagold varieties at 5% significant level.*

| Variety | Golden Delicious | Jonagold | Overlapping |
|---|---|---|---|
| Golden Dlicious | 90% | --------- | 10% |
| Joangold | 3.3% | 83.4% | 13.3% |

- All the range of NIR used (700-1100 nm) have modeling power in each variety. The range that has the discrimination power between varieties was 1050-1100 nm.

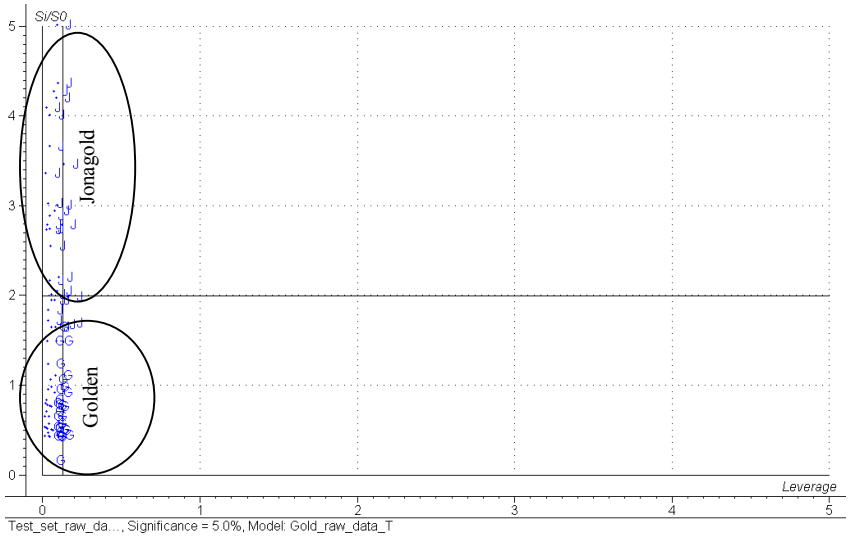


*Fig. 3. The relative distance vs. leverage plot (Si/S0 vs. Hi) for train set of Golden Delicious vareity model at 5% significant level.*

## 3.2. Aroma and Elstar experiment

- The chemical reference values of 200 apples of both varieties are tabulated in Table 5.

*Table 5. Physical reference values of Aroma and Elstar apples.*

| Variety | SSC (Brix) | | | | Acidity (g/100g) | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean | SDev | CV | Range | Mean | SDev | CV | Range |
| Elstar | 12.21 | 0.61 | 0.05 | 13.9-10.8 | 0.89 | 0.08 | 0.09 | 0.72-1.09 |
| Aroma | 12.16 | 0.61 | 0.05 | 14-10.7 | 0.90 | 0.06 | 0.07 | 0.76-1.06 |

- The SSC and acidity were insignificantly different between both varieties at 5% significant level.
- The correlation coefficients between SSC and acidity was very low (47.5%).
- PLS-1 was used for modeling SSC and acidity using raw NIR reflectance for both varieties. For calibration, 140 samples were used. For validation 60 samples were used. The modeling for SSC and acidity was not reliable in this experiment. The best model for SSC has RMSEP of 0.48 and about 60% correlation for validation set. Modeling Elstar's SSC alone was reasonably good, hasing a validation correlation of 73%. Figure 4 shows the averaged reflectance for Elstar and Aroma varieties.

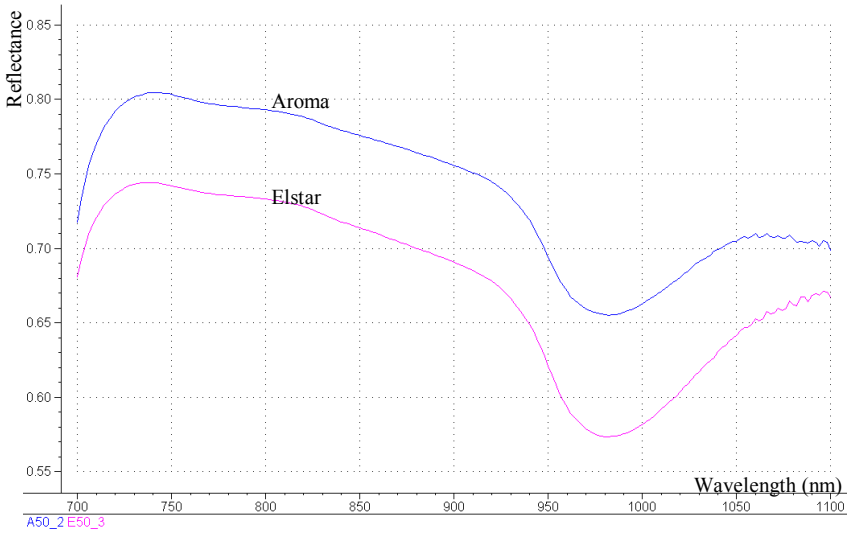


*Fig. 4. Mean reflectance (raw data) of Aroma and Elstar varities.*

- The second derivative pre-processing technique was used for classification process. Quite distinguished groups (varieties), along the first principal component, were clearly noticed in Fig. 5.

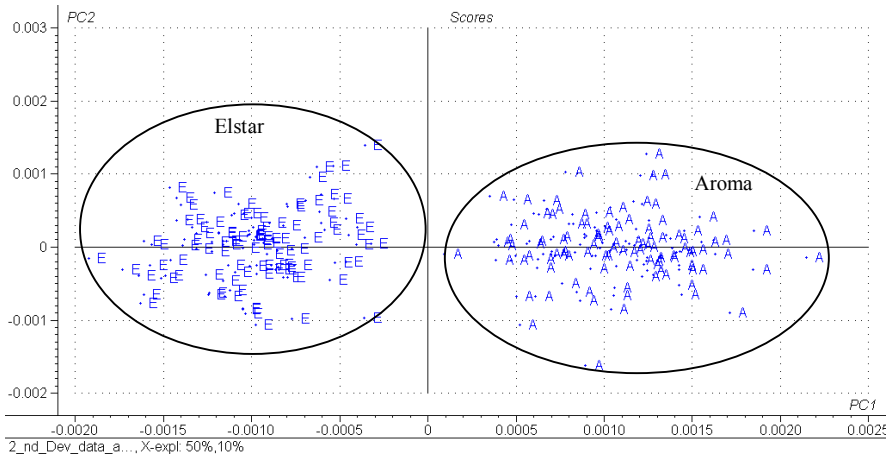


*Fig. 5. Reflectance spectra scores plot for all Elstar and Aroma samples. Distinguished groups (A: Aroma, E: Elstar) are clearly seen along the first principal component.*

- SIMCA was used for classification. Considering all apple samples, a training set of 70 samples and test set of 30 samples for each variety were used. Full cross validation was used for building the principal components models for each variety. The discrimination results are shown in Table 6. The coomans plot (objects to model distance) for all Aroma and Elstar apples at 10% significant level is shown in Fig. 6. This plot shows that all Elstar samples are classified uniquely as belonging to Elstar model, as well as Aroma samples belonging to Aroma model.

*Table 6. Classification results for all samples of Aroma and Elstar at different significant level.*

| Significant level | Variety | Aroma | Elstar | Overlapping |
|---|---|---|---|---|
| 5% | Aroma | 94.6% | ------- | 5.4% |
| | Elstar | --------- | 81.1% | 18.9% |
| 10% | Aroma | 100% | ------- | --------- |
| | Elstar | ------- | 97.3% | 2.7% |

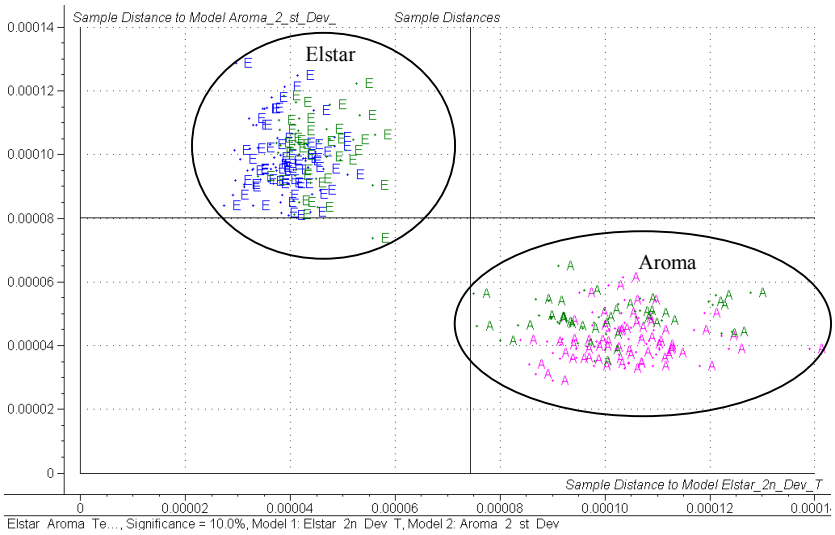


*Fig. 6. Coomans plots for all Aroma and Elstar samples (train and test sets) at 10% significant level.*

- Samples having the same SSC/acidity values, within ±5%, were selected yielding 123 samples from both varieties. For classification of these samples, 40 and 20 samples were used for train set and test set respectively for each variety. Table 7 shows the results of SIMCA classification at 10% significant level. Figure 7 shows the coomans for all Aroma and Elstar apple samples that have the same ratio of SSC and acidity.

*Table 7. SIMCA's classification result of all Aroma and Elstar samples having the same SSC/acidity values at 10% significant level.*

| Variety | Aroma | Elstar | Overlapping |
|---|---|---|---|
| Aroma | 100% | ----- | ------ |
| Elstar | ----- | 85% | 15% |

- The modeling power wavelengths for classification models of both varieties were 700-750 nm and 1050-1100 nm. While the discrimination power wavelengths was not identified by a range, different wavelengths has discriminant power and among these are: 730-734, 742-748, 768-790, 814, 822-826, 840, 860-862, 866-874, 922-924, 1036-1038 and 1076 nm.

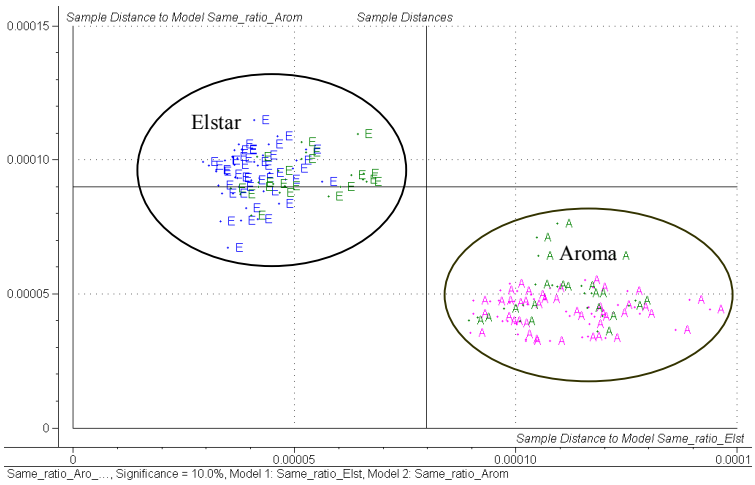


*Fig. 7. Coomans plot for all Aroma and Elstar samples (train and test sets) having the same ratio of SSC and acidity at 10% significant level.*

# 4. Discussion

## 4.1. Golden Delicious and Jonagold varieties

1. There was a good correlation between a number of the quality parameters. SSC and acidity were highly correlated, while the firmness was not reasonable correlated either with SSC or acidity. This is normal, since firmness is difficult to be predicted using SSC and acidity.
2. The samples of both varieties were homogenous in terms of SSC, acidity and firmness, since the CV (coefficient of variation) was small and about the same in both varieties.
3. Using 140 apples for calibration is reasonable. Since six was the maximum latent variables number used to construct the calibration model. This is in agreement with a statistical rule of thumb, which states that the ratio of the number of samples to the numbers of variables should be equal to or larger than ten. [2] There are still about twenty times more samples than latent variables (principal components) in our models.
4. The prediction of apples' SSC, which has a correlation of 82% and six latent variables, was quite reliable. Bellon [9] built a SSC model with five latent variables between predicted and measured SSC values of 85%. Lammertyn *et al.* [10] obtained correlation coefficients for SSC predictions between 80%-90%, depending on the number of PCs and the pre-processing techniques. Moons *et al.* [11] got a correlation greater than 80% for SSC prediction.
5. Acidity correlation was also reliable.
6. No reliable relationship was found between firmness and NIR spectrometer. Kupferman [12] stated that fruit firmness is generally very difficult to model, since many factors are involved. Theoretically it is possible that scattering of light within the fruit may related to firmness.

7. Classification of Golden Delicious and Jonagold was reasonable good, clear distinguished groups can be seen in the relative distance versus leverage plot (Fig. 3) indicating a successful classification process. Golden Delicious and Jonagold were correctly classified in 90% and 83.4% of the cases respectively at 5% significant level. The overlapping is normal and expected, taking into consideration the inherent relationship between both varieties. Jonagold is a hybrid from Golden Delicious and Jonathan.
8. Unfortunately, there were no enough samples that had the same SSC/acidity values to run the classification on those samples. The above classification result took all taste components (SSC, acidity and characteristic taste parameters) into consideration. This indicates that NIR technique has a high potential for detecting different varieties of fruits.
9. All the range of NIR can be considered as having discrimination power, since the photo diode array has a lower sensitivity for high wavelengths (1050-1100 nm).

## 4.2. Aroma and Elstar varieties

1. NIR was not able to model SSC and acidity for both varieties with a reliable correlation. For Elstar itself, it was possible to model SSC with a validation correlation of 73%. It was noticed that some of the Aroma samples were overripe, which may cause the failure of SSC and acidity models. Over ripening of Aroma can be explained by the fact that Aroma is an earlier variety, while Elstar is picked later than Aroma.
2. The samples of both varieties were homogenous in terms of SSC, acidity and firmness, since the CV was small and about the same in both varieties.
3. SIMCA was able to classify Elstar and Aroma with a high performance at different significant levels. Clear distinguished groups can be seen in coomans plot (Fig. 6). Aroma and Elstar were correctly classified in 94.6% and 81.1% of the cases respectively at 5% significant level. A relatively slight overlapping occurred. That was expected due to the morphology of apples.
4. Considering samples having the same SSC/acidity values, classification result was reasonable good. Aroma and Elstar were classified correctly in 100% and 85% cases respectively at 10% significant level. The overlapping indicates that some of the characteristic taste parameters between two varieties are common.
5. The different wavelengths, which have the discriminant power between both varieties, should be investigated more to know the chemical composition of materials causing this discrimination.
6. A good classification has been achieved between two different apple varieties, even when they have the same SSC/acidity values. Human sensory was not used for collecting data neither for data analysis. This gives NIR technique a global (standard) method for taste sensing.

## 5. Conclusion

Results from these experiments indicate that:

1. In general terms, NIR is able to predict quality parameters; like SSC and acidity, with an acceptable range when having a very good spectrometer stability versus time and temperature;
2. NIR spectroscopy is able to detect the different varieties of apples with a high performance, which indicates that NIR can sense the overall taste of fruit;
3. Furthermore, NIR spectroscopy is able to detect different varieties of apples even when they have the same ratio of SSC and acidity; this indicates that NIR can detect the characteristic taste parameters of each variety;
4. Further research is needed to study the wavelengths that contribute in the discrimination between two apples' varieties having the same ratio of SSC and acidity;
5. NIR technique can be used as a global (standard) method for sensing taste; and
6. The overall conclusion is that NIR technique has a high potential for sensing taste of fruits.

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# 7. Perspectives

This study is a modest contribution to postharvest technology, it is a step in a long research process, for sensing fruits' taste and for investigating the characteristic taste parameters for each fruit's variety.

In this study, it was concluded that NIR spectroscopy has a high potential to detect taste of fruits. Furthermore, NIR technique can be used as a global (standard) method for sensing taste.

Further research and investigation is needed to be carried out to study:

- The exact chemical composition of characteristic taste parameters that distinguish between two fruit varieties; and
- The development of characteristic taste parameters during maturity in each fruit.

A Ph.D. research may be needed for further investigation.

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# Appendix

*This appendix includes glossaries of statistical terms that are important to understand the multivariate analysis, and mostly used or mentioned in this thesis. These terms are:*

## *Chemometrics:*

Discipline concerned with the application of statistics and mathematical methods of chemistry. It is now recognized as a branch of analytical chemistry. This word is juxtaposition of chemo (*latin,* chemistry) and metrics (*greek,* measure) (Andersen, 2000).

The difference between statistics and chemometrics is:

'The aim of a statistician is to reduce the information in a set of data to a small number of statistical variables, which summarize the relationship between various sets of data. He may have no knowledge of chemistry or instrumentation. A chemometrician brings knowledge of the chemical and sometimes the instrumental influences, which effect the data. The aim here is often to display the data in ways that allow chemical interpretation of the system. This may involve transformation the data in ways, which brings out features which, were not evident from the raw data or deriving new variables which are functions of the original data. Chemometricians make their living by adding value to the process of statistical analysis by bringing in skills which statisticians lack' (Davies, 1998).

## *Multivariate:*

A multivaratie measurement is when more than one variable or response is measured for each sample of interest (Esbensen *et al.*, 2000).

## *PCA:*

It is a multivariate analysis that reduces dimensional space without losing information. This bilinear modeling method gives an interpretable overview of the main information in a multidimensional data set. The original variables' information is projected onto a smaller number of underlying variables (latent variables) that called principal components. The 1$^{st}$ principal component covers as much as possible the variation in the data. The 2$^{nd}$ principal component covers as much as possible of the remaining variations and it is orthogonal to the 1$^{st}$ principal component. Interrelationships between different variables, grouping, similarities, differences,

detecting and interpreting samples pattern can be got by plotting the principal components (Esbensen *et al.*, 2000).

## *PCs:*

'They are composite variables, since they are linear functions of the original variables, estimated to contain, in a decreasing order, the main structured information it the data. They are also called a latent variable and a PC is the same as a score vector. PCs are estimated in PCA and PCR. PLS components are also denoted PCs' (Esbensen *et al.*, 2000).

## *Model:*

Mathematical equation summarizing variation in a data set. They are built to make it easier to understand the structure of the data. Statistical models consist of two parts:

1. A structure part (information): that can be used for interpretation or prediction; and
2. Error part (noise): this part should be as small as possible to consider the model as reliable. The purpose of multivariate modeling is to separate information from noise (Esbensen *et al.*, 2000).

Choosing the best model is diffucult, since it depends on a number of parameters and aslo depend on the goal of analysis. Generally, the best models in Unscrambler statistical software package are the models which have (Lammertyn *et al.*, 2000; Piers *et al.*, 2000):

1. Low RMSEP;
2. High correlation coefficient (r) between the predicted and the measured values;
3. Low no. of latent variables; and
4. Low difference between RMSEP and RMSEC values, since a large difference indicates that the calibration set doesn't represent the validation set.

## *Noise:*

' Random variation that does not contain any information' (Esbensen *et al.*, 2000).

## *Calibration:*

'Stage of data analysis where a model is fitted to the available data, so that it describes the data as good as possible. After calibration, the variation in the data can be expressed as the sum of a modeled part (structure) and a residual part (noise)' (Esbensen *et al.*, 2000).

## *Validation:*

'Validation means checking how well a model will perform for future samples taken from the same population as the calibration samples. In regression, validation also allows for estimation of the prediction error in future prediction. The outcome of the validation stage is generally expressed by a validation variance. The close the validation variance is to the calibration variance, the more reliable the model conclusions. When explained validation variance stops increasing with additional model components, it means that the noise level has been reached. Thus the validation variance is a good diagnostic tool for determining the proper number of components in a model. Validation variance can also be used as a way to determine how well a single variable is taken into account in an analysis. A variable with a high explained validation variance is reliably modeled and is probably quite precise; a variable with a low explained validation variance is badly taken into account and is probably quite noisy. Three validation methods are available in The Unscrambler multivariate analysis program:

1. Test set validation;
2. Cross validation; and
3. Leverage correction' (Esbensen *et al.*, 2000).

## *Test set validation:*

'Validation method based on the use of different data sets for calibration and validation. During the calibration stage, calibration samples are used. Then the calibration model is used on the test samples, and the validation residual variance is computed from their prediction residuals' (Esbensen *et al.*, 2000).

## *Cross validation:*

'Validation method where some samples are kept out of the calibration and used for prediction. This is repeated until all samples have been kept out once. Validation residual variance can then be computed from the prediction residuals. In segmented cross validation, the samples are divided into subgroups or segments. One segment at a time is kept out of the calibration. There are as many calibration rounds as segments, so that predictions can be make on all samples. A final calibration is then performed with all samples. In full cross validation, only one sample at a time is kept out of the calibration' (Esbensen *et al.*, 2000).

## *Leverage correction validation:*

'A quick method to simulate model validation without performing any actual predictions. It is based on the assumption that samples with a higher leverage will be more difficult to predict accurately than more central samples. Thus a validation residual variance is computed from the calibration sample residuals, using a correction factor which increases with the sample leverage. This method should be used as a quick and dirty method for a first calibration, and a proper validation method should be employed later on to estimate the optimal number of components correctly' (Esbensen *et al.*, 2000).

## *MLR:*

It is a method for relating the variation in a response variable (Y-variable) to the variations of several predictors (X-variables), with predictive or explanatory purposes. For this method it is important to assume that there is no collinearity between the X-variables (X-variables should be linearly independent) (Esbensen *et al.*, 2000).

## *PCR:*

'It is a method for relating the variation in a response variable (Y-variable) to the variations of several predictors (X-variables), with explanatory or predictive purposes. This method performs particularly well when there is a large amount of correlation or even collinearity (linear relationship between variables, linear dependant between variables). PCR consists of a two-step method:

$1^{st}$: PCA is carried out on the X-variables; and

$2^{nd}$: the PCs are used as predictors in a MLR' (Esbensen *et al.*, 2000).

## *PLS:*

'PLS is a multivariate full-spectrum regression technique, which was primarily designed for causal-predictive analyses of complex problems that are rich in data but scarce in theoretical knowledge' (Peires, 1998).

'A method relating the variations in one or several response variables (Y-variables) to the variations of several predictors (X-variables), with explanatory or predictive purposes. This method performs particularly well when the various X-variables express common information, i.e. when there is a large amount of correlation, or even collinearity. Partial Least Squares Regression is a bilinear modeling method where information in the original X-data is projected onto a small number of underlying (latent) variables calls PLS components. The Y-data are actively used in estimating the latent variables to ensure that the first components are those that are most relevant for predicting the Y-variables ' (Esbensen *et al.*, 2000).

'PLS is well established with NIR, since NIR applications often require methods based on many wavelengths due to non-selective and full-spectrum wavelength responses' (Esbensen *et al.*, 2000).

The advantages of PCR and PLS techniques over MLR are (Bellon and Sevila, 1993):

1. No wavelength selection is needed;
2. The variables are orthogonal, causing stability in the matrix inversion; and
3. The information is not redundant.

The advantage of PLS over PCR is (Lammertyn *et al.*, 1998):

PLS models don't include the latent variables that are not important to describe the variance of desired parameters, which means that PLS models will have the lowest number of variables.

## *PLS1:*

'Version of the PLS method with only one Y-variable' (Esbensen *et al.*, 2000).

## *PSL2:*

'Version of the PLS method in which several Y-variables are modeled simultaneously, thus taking advantage of possible correlation or collinearity between Y-variables' (Esbensen *et al.*, 2000).

## *Correlation:*

'A unit-less measure of the amount of linear relationship between two variables. The correlation is computed as the square root of the covariance between the two variables divided by the product of their variances. It varies from –1 to +1. Positive correlation indicates a positive link between the two variables, i.e. when one increase the other has a tendency to increase too. The closer to +1, the stronger this link. Negative correlation indicates a negative link between the two variables, i.e. when one increase the other has a tendency to decrease. The closer to -1, the stronger this link' (Esbensen *et al.*, 2000).

## *RMSEC:*

'A measurement of the average difference between predicted and measured response values, at the calibration stage. RMSEC can be interpreted as the average modeling error, expressed in the same units as the original response values' (Esbensen *et al.*, 2000).

Mathematically it can be described as (Lammertyn *et al.*, 2000):

$$RMSEC = \sqrt{\frac{1}{I_c - 1}\sum_{i=1}^{I_c}(\hat{y}_i - y_i)^2}$$

Where: $\hat{y}_i$ = predicted value of the i-th observation;

$y_i$ = measured value of the i-the observation; and

$I_c$= no. of observations in the calibration set.

## *RMSEP:*

'A measurement of the average difference between predicted and measured response values, at the validation stage. RMSEP can be interpreted as the average prediction

error, expressed in the same units as the original response values' (Esbensen *et al.*, 2000).

Mathematically it can be described as (Lammertyn *et al.*, 2000):

$$RMSEP = \sqrt{\frac{1}{I_p - 1}\sum_{i=1}^{I_p}(\hat{y}_i - y_i - bias)^2}$$

Where: $\hat{y}_i$ = predicted value of the i-th observation;

$y_i$ = measured value of the i-the observation;

$I_c$ = no. of observations in the calibration set;

$I_p$ = no. of observations in the validation set; and

bias: bias (mentioned below).

Esbensen *et al.*, 2000, stated that SEP and Bias are two statistical measures closely linked to RMSEP, since:

$$RMSEP^2 \approx SEP^2 + Bias^2.$$

Also: *2* RMSEP = estimated precision when predicted y-values.*

## *SEP:*

'Variation in the precision of prediction over several samples. SEP is computed as the standard deviation of the residuals'.

*2*SEP = 95% confidence interval* (Esbensen *et al.*, 2000).

$$SEP = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y} - y_i - Bias)^2}{n-1}}$$

## *Bias:*

It is the average difference between predicted and measured Y-values for all samples in the validation set. It is used to check if there is a systematic difference between the average values of the training set and the validation set. If there is no difference the *Bias* will be zero (preferable condition) (Esbensen *et al.*, 2000).

Mathematically it can be described as (Lammertyn *et al.*, 2000):

$$Bias = \frac{1}{I_p}\sum_{i=1}^{I_p}(\hat{y}_i - y_i)$$

## *SEC:*

Mathematically it can be expressed as (Schmilovitch *et al.*, 2000):

$$SEC = \sqrt{\frac{\sum(\hat{Y} - Y)^2}{N - 2}}$$

Where:Y= the actual value of the sample;

$\hat{Y}$=the calculated (predicted) value of the sample; and

N= no. of samples.

It is expressed in the same units as the original parameters.

## *SIMCA:*

'Classification method based on disjoint PCA modeling. SIMCA focused on modeling the similarites between members of the same class. A new sample will be recognized as a member of a class if it is similar enough to the other members; else it will be rejected'. The advantages of SIMCA are:

1. SIMCA is not restricted to situation in which the no. of objects is significantly larger than the no. of variables;
2. Collinearities (linear relationship between variables) can be handled easily;
3. SIMCA is ralatively easy to use for multi-class belonging purpose; and
4. SIMCA displayes all pertinent rasults graphically with exceptional insight regarding the specific data structure behind the modeled pattern (Esbensen *et al.*, 2000).

***References related to appendix***

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